Explorations of Thermodynamics and Information in Quantum Field Theory

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Abstract

Thermodynamics has arguably been one of the most powerful branches of physics, and the most universal in its breadth of applications. From steam engines to black holes, the laws of thermodynamics seem to rule it all.

However, even the most basic concepts in thermodynamics quickly become problematic in quantum theory. Defining simple notions such as work is actually an open problem with multiple incompatible answers. It gets worse: the most accepted definition of work in quantum thermodynamics, the two-point measurement scheme (TPM), generally violates the first law. When looked at from the perspective of quantum field theory, the situation gets even worse since the TPM scheme becomes ill-defined.

We will analyse alternative definitions of work distributions for quantum field theory that are a) well defined b) physically understandable c) amenable to computations in a non-perturbative way and d) fulfil the first law of thermodynamics on average and in variance as well as some of the most important non-equilibrium theorems such as Crooks theorem and the Jarzinsky equality. We will show how, for KMS (thermal) states, we can provide the exact statistics of work and energy increase for unitary operations on the quantum field which are localized in space and time.

Keywords: First Law of Thermodynamics, Quantum Field Theory, Quantum Thermodynamics, Work Distribution, Fluctuation Theorems, KMS state, Particle Detector, Two-Point Measurement Scheme, Quasi-probability.

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Published content

As a result of this Bachelor's degree research project we are preparing an article with the authors Alvaro Ortega and Eduardo Martín-Martínez, of tentative title *The first law of quantum field thermodynamics*, for the journal Pysical Review Letters.

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Chapter 1

Introduction

1.1 Motivation

In the study of systems comprised of a small number of particles, or that are outside of thermal equilibrium, average quantities of physical observables are no longer enough to completely characterize their state or the features of their evolution. In this regime, stochastic and quantum fluctuations can be of the same order of magnitude of the expectation values [1, 2, 3], so we need to take them into account in order to have a complete understanding of the thermodynamic properties of the system.

One of the most important and best studied quantities in this context is work of out-of-equilibrium processes and its fluctuations. However, understanding the notion of work in quantum systems is a notoriously difficult task, since it cannot be associated to an observable [4]. Several ways to define work fluctuations have been proposed [5], each of which gives different pieces of information about the thermodynamics of adiabatic processes in quantum systems. One of the most established notions of work fluctuations comes from the Two-Point Measurement (TPM) work distribution [5, 6, 7]. The TPM work distribution of a process is obtained by performing two projective measurements of the system's energy at the beginning and at the end of the process. However, as it was discussed in [8] it is not possible to readily extend the definition of TPM work distribution to quantum field theory (QFT). This is due to the fact that projective measurements are ill-defined in QFT, breaking relativistic covariance, having spacetime localization problems, and introducing UV divergences [9, 10, 11, 12].

Defining work distributions in QFT is challenging. Since projective measurements are not compatible with QFT, the only way to extract information about the field is by coupling local probes to the field and then measuring those local probes [13, 8, 14]. Additionally, there is no well-defined notion of Gibbs thermality for a quantum field: QFT entropies at constant energy can be divergent and partition functions are not well-defined in QFT in free space. The right notion of thermality for QFT is captured by the much more general notion of the Kubo-Marting-Schwinger (KMS) conditions [15, 16]. Not being able to assume Gibbs thermality makes it harder to prove general theorems about thermal states (such as the fluctuation relations [1, 2, 7]) in scenarios involving quantum fields. Moreover, performing concrete calculations is notoriously hard in QFT, and in most cases these can only be done perturbatively.

Last year, in [8] a first valid definition of work distribution for quantum fields inspired by interferometric schemes was introduced, and some of its main properties, such as fluctuation relations and the relationship between fluctuations and expected values in different regimes were studied. This primed the question of whether the first law of thermodynamics is true for quantum fields, with this definition of work.

1.2 Aims and Objectives

The objectives of this exploration are to answer:

1. Is the first law of thermodynamics true in QFT?

2. Could work distributions previously presented in a non-relativistic setting be meaningful in QFT?

The second question originated when it became clear that the first law of thermodynamics was true in QFT, at least in average, for the first valid work distribution on quantum fields [8] (which we will refer to as Ramsey scheme work distribution).

1.3 Description of the thesis

First, we present the theoretical frame used to develop this thesis, we start with quantum thermodynamics, going through the concept of fluctuating work, the difficulties to characterize it and the motivations to characterize it as a quasi-probability work distribution. Next, we expose the usefulness of quasi-probabilities in quantum mechanics. We finish the presentation of the theoretical frame with an overview of QFT: the formalism for performing calculations on free scalar fields, the concept of detectors and describe KMS thermality.

Second, we describe the methodology that we used to answer the two objectives asked above. We use two methods: 1) Compute the first law of thermodynamics in a QFT setting and observe coincidence or deviations. The specific setting was a family of unitary processes on free scalar quantum fields and KMS states. 2) Search for work distributions, aside from [8], that meet a list of requirements motivated by thermodynamics (relatability to the classical work probability distribution) and by compatibility with QFT. Work distributions that fulfill these requirements are meaningful in QFT.

Third, we present the results found from the two methods. We provide the work distributions that are meaningful for QFT (method 2) and then use them to compute the first law of thermodynamics on a quantum field (method 1). In the same chapter we deepen the study of the Ramsey scheme work distribution, showing it is a quasi-probability distribution, that can attain complex values when the initial state has coherences in the energy eigenbasis. This turns out to be a necessary consequence of the no-go theorem [17]. We also compare the moments of the work distribution and the internal energy difference distribution, the average coincides (the first law is satisfied on average) but discrepancies arise for the higher moments (which can also be seen as a consequence of the no-go theorem). We prove Crooks theorem for cyclic unitary processes of QFT, for KMS states. Remarkably, we obtain exact, non-perturbative, expressions for the work distribution associated to the family of space-time localized unitaries of method 1).

Lastly, we discuss the implications of results in a wide context and conclude with a summary of the results.

1.4 Sources, methodology and project stages

The project had four stages,

1. Learning the basic background concepts to understand the project. I viewed the online classes of the course of Relativistic Quantum Information of the University of Waterloo, by the supervisor of this thesis, Eduardo Martín-Martínez. Moreover, I went through a guided list of articles on quantum thermodynamics (including parts of the reviews [18, 5, 19]) that served to understand the article about the first work distribution on quantum fields [8]. The first author of the article, Alvaro Ortega, provided me the list.

2. The computation of the first law of thermodynamics for a quantum scalar field, with the work distribution and the processes presented in [8].

3. The search for proposals of work distributions that were compatible with a list of requirements that we confected. Those were requirements to be applicable to QFT and obtain there the first law of thermodynamics. The source used was a list of proposals for fluctuating work [5] and the references contained in it.

4. Writing part of the results, together with the supervisor and one of its former students Alvaro Ortega, as a scientific article that will be send for peer review to Physical Review Letters, under the tentative title *The first law of quantum field thermodynamics*.

The completion of the fourth stage will continue after the moment of uploading this thesis.

Chapter 2

Background and Related Work

2.1 Quantum Thermodynamics

Quantum thermodynamics is a field undergoing fast development and will become important to develop efficient engines and batteries at the molecular scales [20]. We expose the results of quantum thermodynamics which will be relevant for this thesis, revolving around the notion of fluctuating work. We start from a reminder of classical concepts and transition to the quantum scenario to see what we keep and what is new.

2.1.1 Macroscopic Work and Heat

In our macroscopic world, work and heat are quite familiar concepts. Work (W) is associated to exchange of useful energy, in a controlled manner, while heat (Q) is an uncontrolled exchange of energy, which is not useful on its own, but whose flow can be used to generate work. They are related by the first law of thermodynamics, which we usually regard as the conservation of energy,

$$\Delta U = W + Q. \tag{2.1}$$

Where ΔU is the difference of internal energy of a system before and after a process. The process performed work W on and transmitted heat Q to the system. The first law, as fundamental as it seems, breaks down in quantum thermodynamics for some existing notions of quantum fluctuating work [5], as we tackle below. However, as we explore in this thesis, there is a first law of thermodynamics, at least for unitary (thus adiabatic) processes, even in the relativistic settings of Quantum Field Theory (QFT).

Back to the classical macroscopic scenario, W and Q depend on the process because they are not state functions. However, each time we repeat a process the answer will be the same, up to error which is bound to happen in the experimental setup. The averages of W and Q will be enough to characterize the energy exchanges of the process. The reason is that our processes are in the thermodynamic limit (large number of particles). This is the first property that we lose in our exploration.

2.1.2 Fluctuating Work

The systems with a small number of particles have stochastic fluctuations [3], averages are no longer enough. We now illustrate why, picture a chamber with a mobile wall (a piston), filled with air. Push the piston to compress the air, applying work. Now decrease the number of air particles until the extreme case of one particle. The same push of the piston will perform a different work depending on where the particle is and is heading at the start of the process. We do not know this information and deem it as stochastic.

Statistical thermodynamics assigns probability distributions to W and Q to model these fluctuations. Their definitions can be found in [5, 18]. However, these definitions do not apply to quantum mechanics, because they assume the states of the system have a definite energy at every instant. Oppositely, quantum states that do not commute with the Hamiltonian do not have definite energies. This entails another source of fluctuations, of purely quantum origin, when we try to determine the energies through measurement.

2.1.3 Fluctuation Theorems

The development of the fluctuation theorems is a quite recent milestone of statistical thermodynamics [21], which improves the understanding of irreversible processes. They tie fluctuations of out-of-equilibrium processes to equilibrium quantities.

For work, we have Crooks theorem [22] and Jarzynski equality [23]. The Crooks theorem relates the work probability distribution $P(W)$ of a process with the work probability distribution of the process done in reverse $P_{rev}(W)$. Both the process and the reverse process must start with the system in a thermal state of inverse temperature β. The expression for Crooks theorem is [18, 24]

$$\frac{P(W)}{P_{rev}(-W)} = e^{\beta(W-\Delta F)}. \tag{2.2}$$

Where ΔF is the free energy difference between the initial and final state of the system. Crooks theorem implies the earlier Jarzynski equality [18],

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}. \tag{2.3}$$

Jensen's inequality $\left\langle e^{-\beta W} \right\rangle \geq e^{-\beta \langle W \rangle}$ can derive from it

$$\langle W \rangle \geq \Delta F, \tag{2.4}$$

which is the second law of thermodynamics. As pointed out in [18] Jarzynski equality strengthens the second law, involving all the moments of work.
Both theorems were used to estimate ΔF in stretched molecules [25], they improve the estimation because experimental measurement processes usually bring the system out of equilibrium.
The work fluctuation theorems were brought to quantum thermodynamics [6], with some caveats, as we will discuss below.

2.1.4 Quantum fluctuating work

In quantum thermodynamics we deal with systems of a small number of particles, which means that work should have both stochastic and quantum fluctuations. However, defining fluctuating work in this context is difficult, there are multiple proposals [5], no one is perfect [17], and each might provide complementary information about fluctuations. This multiplicity is directly related to the idea that work is not an observable of the system [4], which forces us to specify the measurement scheme for work. The choice of measurement scheme will influence the outcome and implicitly define an instance of fluctuating work. Historically, the first proposal of fluctuating work is the so called operator of work $\hat{W}$, defined for unitary processes (which are adiabatic, $Q = 0$) by imposing the first law $\hat{W} = \Delta\hat{U}$. $\Delta\hat{U}$ is the internal energy difference operator,

$$\Delta\hat{U} = \hat{U}^\dagger \hat{H}_\tau \hat{U} - \hat{H}_0 \,. \tag{2.5}$$

where $\hat{U}$ is the unitary operator of the process, $\hat{H}_0$ the system Hamiltonian at the start of the process and $\hat{H}_\tau$ the system Hamiltonian at the end of the process. The probability distribution of $\hat{W}$ is extracted through the usual Born's rule. $\hat{W}$ immediately satisfies the first law but does not properly reflect fluctuations [26, 5], neither fulfills the fluctuation theorems [5].

The fluctuation theorems were successfully exported to quantum thermodynamics [6] by defining fluctuating work as the difference between two projective measurements of the internal energy, the TPM (Two Point Measurement) scheme. Concretely the TPM work probability distribution is obtained through the protocol [5]:

1. Projectively measure $\hat{H}_0$ on the initial state of the system $\hat{\rho}$, obtaining outcome ϵ_i and as post-measurement state $|\epsilon_i\rangle\!\langle\epsilon_i|$.

2. Evolve $|\epsilon_i\rangle\!\langle\epsilon_i|$ with the unitary $\hat{U}$.

3. Projectively measure $\hat{H}_\tau$ on $\hat{U}^\dagger|\epsilon_i\rangle\!\langle\epsilon_i|\hat{U}$, obtaining outcome ϵ'_j.

Here, the work performed is $W = \epsilon'_j - \epsilon_i$, and the joint probability of the outcomes provides the work probability distribution

$$P_{\text{TPM}}(W) = \sum_{i\,j} \langle\epsilon_i|\hat{\rho}|\epsilon_i\rangle \left| \left\langle\epsilon_i\middle|\hat{U}\middle|\epsilon'_j\right\rangle \right|^2 \delta\big(W - (\epsilon'_j - \epsilon_i)\big) \tag{2.6}$$

The TPM scheme provides the right notion of fluctuations, at least when $\left[\hat{\rho}, \hat{H}_0\right] = 0$ (otherwise, coherence of $\hat{\rho}$ on the eigenbasis of $\hat{H}_0$ gets simply erased by the first projective measurement). However, the first law of thermodynamics is not valid for the TPM scheme, and there are states for which the first law is violated in expectation, among the states $\left[\hat{\rho}, \hat{H}_0\right] \neq 0$. This is no coincidence, but rather a general statement for quantum work probability distributions, as we expose below.

2.1.5 The No-go Theorem for Characterization of Fluctuating Work

We might hope that among the multiple proposals of fluctuating work there is one that keeps the properties of classical fluctuating work. Specifically, we might try to find a notion of fluctuating work for unitary processes for which:

1. The work is a probability distribution.
2. The work is the TPM work distribution for states $\left[\hat{\rho}, \hat{H}_0\right] = 0$, thus guaranteeing the satisfaction of the fluctuation theorems.
3. The first law of thermodynamics is true in expectation.

Features that are true for classical fluctuating work. However, it is impossible to have them simultaneously for quantum thermodynamics, according to the no-go theorem for the characterization of work fluctuations [17].
We drop the assumption that work is a probability distribution in the present exploration, because the other two conditions are grounded on thermodynamics. Instead we will consider work to be a quasi-probability distribution, concept that we explore next.

2.2 Quantum Information

2.2.1 Quasi-probability Distributions of Work and Joint Distributions of Non-Commuting Operators

Quasi-probability work distributions are able to satisfy the fluctuation theorems (through coinciding with the TPM distribution on states $\left[\hat{\rho}, \hat{H}_0\right] = 0$) and the first law of thermodynamics in expectation. They are not limited by the no-go theorem described above because they are not probability distributions. Indeed, there are proposals of quasi-probability work distributions in the literature [26, 27, 28] which satisfy both fluctuation theorems and the first law.

We can extract the moments of work from its quasi-probability distribution, as can be done for any distribution. The difference with a probability distribution is that it can take negative or even complex values. However it keeps normalization (integrates to 1) and linearity with respect to the state $\hat{\rho}$ of the system at the start of the process whose work we are assessing. This linearity assures that when we mix two states $\hat{\rho}_1$ and $\hat{\rho}_2$ (e.g. choosing between them at the start of the process according to a coin flip) the quasi-probabilities behave as we would expect if they were probabilities.

Using quasi-probabilities is not new in quantum mechanics, but rather the opposite. Quasi-probabilities have been used to define joint distributions for non-commuting observables [29, 30, 31, 32, 33, 34, 35], among them the Wigner function (1932) allows for the phase-space representation of quantum mechanics. Probability distributions are recovered when taking marginals, for instance when restricting to one observable.

Remarkably, some quasi-probability distributions have an intimate relation to the foundations of quantum mechanics, they distinguish between processes that could be explained with a classical theory (non-contextual), and ones that not (contextual). Particularly, the negativity of the quasi-probability work distribution proposed by Allahverdyan [26] has been shown to be equivalent to contextuality [36].

2.3 Quantum Field Theory

QFT appeared from the effort to obtain a relativistic quantum theory. It is the base theory for the present Standard Model of particle physics which describes three of the four fundamental forces, electromagnetism, weak and strong forces, with big success in giving precise predictions (as the anomalous moment of the electron). However, it is a theory that still lacks understanding. Thermodynamics are in development for it, the last year the first proposal of work distribution was successfully brought to the QFT formalism [8]. This motivates the exploration of thermodynamics of QFT and search for more work distributions fit for QFT in this research. We present the formalism of free scalar quantum fields because we performed concrete calculations about the thermodynamics of their unitary processes. We also present the correct way to tackle particularities of QFT that can make a quantum work distribution ill-defined and that are (usually) not present in quantum mechanics.

2.3.1 Free Scalar Field

We provide here the QFT formalism of the calculations made in this research work about scalar fields. We give the expression of the Hamiltonian when they are not interacting, i.e. when they are free, as a function of the field operator and its canonical momentum, which we also describe.

A free scalar field can be pictured as the space filled with coupled harmonic oscillators extending in all the tree spatial dimensions. The intensity of this field at each point of space is given by the field operator,

$$\hat{\phi}(t, \boldsymbol{x}) = \int \frac{\mathrm{d}^3\boldsymbol{k}}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}} \left(e^{-\mathsf{ik}\cdot\mathsf{x}}\hat{a}^\dagger_{\boldsymbol{k}} + e^{\mathsf{ik}\cdot\mathsf{x}}\hat{a}_{\boldsymbol{k}}\right), \tag{2.7}$$

$$\mathsf{k}\cdot\mathsf{x} = \boldsymbol{k}\cdot\boldsymbol{x} - \omega_{\boldsymbol{k}}t\,, \quad \omega_{\boldsymbol{k}} = \sqrt{m^2 + |\boldsymbol{k}|^2}\,. \tag{2.8}$$

Where m is the mass of the field and $\hat{a}_{\boldsymbol{k}}$ and $\hat{a}^\dagger_{\boldsymbol{k}}$ are the annihilation and creation operators for the field mode $\boldsymbol{k}$, which obey

$$[\hat{a}_{\boldsymbol{k}}, \hat{a}_{\boldsymbol{k}'}] = \left[\hat{a}^\dagger_{\boldsymbol{k}}, \hat{a}^\dagger_{\boldsymbol{k}'}\right] = 0, \qquad \left[\hat{a}_{\boldsymbol{k}}, \hat{a}^\dagger_{\boldsymbol{k}'}\right] = \delta(\boldsymbol{k} - \boldsymbol{k}')\mathbb{I}. \tag{2.9}$$

The field's canonical momentum $\hat{\pi}$ in flat space-time is $\dot{\hat{\phi}}$. The Hamiltonian of a free scalar field is

$$\hat{H}_{free} = \int \mathrm{d}^3\boldsymbol{k}\, \omega_{\boldsymbol{k}}\hat{a}^\dagger_{\boldsymbol{k}}\hat{a}_{\boldsymbol{k}}. \tag{2.10}$$

Importantly, the expression for the field operator (2.7) was given in the Heisenberg image of $\hat{H}_{free}$, i.e. the time evolution due to $\hat{H}_{free}$ is already included in $\hat{\phi}$, which will be practical for the calculations.

2.3.2 The Correct Way of Taking Measurements: Detectors

On quantum mechanics we have on the postulates the prescription of how to take measures. In QFT the prescribed projective measurements are ill-defined. They break the relativistic covariance, allowing for for superluminal signalling, projectors of rank 1 cannot be localized in space-time and they introduce UV divergences [9, 10, 11, 12]. The solution comes from using probes to extract information from the field. This probes are also considered to be quantum systems and extract the information in two steps: 1) Couple the probe, which we can picture as an atom, to the field in a region localized in space-time. 2) Perform projective measurements on the probe, which is a non-relativistic system. The result is that the probe implements certain POVMs on the system. Ultimately, this is the way in which we take measures experimentally, reading the results of a measuring apparatus, not from the system itself. developed to tackle the breakdown of the notion of particle.

Probes were introduced as particle detectors, to provide a well defined the notion of what is a particle in QFT. Specifically, it was used to make more robust the definition of the Unruh effect, which implies that the existence of particles is observer-dependant. Developing the Unruh-DeWitt detector [37, 38, 39] as a result. Moreover, detectors are a focus on Relativistic Quantum Information, e.g. they are used to harvest entanglement from the vacuum or a thermal state of a field [40].

2.3.3 The Correct Way of Defining Thermality: KMS

Gibbs thermality is not always well-defined for QFT, entropy is divergent at constant energy and the partition function is divergent for fields in an unbounded space. Gibbs thermality will also break for other systems where these conditions happen.

There exists a more general notion of thermality, the Kubo-Martin-Schwinger (KMS) thermality, which is equivalent to Gibbs thermality when it is well-defined. For scenarios where Gibbs thermality is ill-defined it recovers the results expected for thermal states, e.g. stationarity for the expectations.

A KMS state [15, 16] of inverse temperature β with respect to a Hamiltonian $\hat{H}$ and a time direction ∂_t is a state $\hat{\rho}_\beta$ for which all pairs of bounded operators $\hat{A}, \hat{B}$, with the definition $\hat{B}(t) = e^{\mathrm{i}t\hat{H}}\hat{B}e^{-\mathrm{i}t\hat{H}}$, satisfy:

1. The expectation values $\left\langle \hat{B}(t)\hat{A} \right\rangle_{\hat{\rho}_\beta}$ and $\left\langle \hat{A}\hat{B}(t) \right\rangle_{\hat{\rho}_\beta}$ are boundary values of some complex functions $\left\langle \hat{B}(z)\hat{A} \right\rangle_{\hat{\rho}_\beta}$ and $\left\langle \hat{A}\hat{B}(z) \right\rangle_{\hat{\rho}_\beta}$ holomorphic in the strips $0 < \mathrm{Im}(z) < \beta$ and $-\beta < \mathrm{Im}(z) < 0$, respectively.

2. Antiperiodicity, $\left\langle \hat{B}(t)\hat{A} \right\rangle_{\hat{\rho}_\beta} = \langle \hat{A}\hat{B}(t + \mathrm{i}\beta) \rangle_{\hat{\rho}_\beta}$.

Chapter 3

Exploration Method

This research followed two methods. The initial method explored the first law of thermodynamics for quantum fields. We checked the first law by computing the quantities involved in it for a general family of unitary processes. The family of processes is interesting because their work (W) distribution has not been computed before. Their work distribution was computed, but perturbatively, on [8].

The second method guided the exploration of work distributions. We assembled a list of requirements that a work distribution must satisfy in order to be meaningful in the context of QFT. The list served two purposes, first, we searched for work distributions compatible with its requirements. Second, the list pointed to interesting properties of these work distributions that were unknown.

3.1 Method to Explore the Thermodynamics of QFT

This method answered whether the first law of thermodynamics could apply to QFT. Also, it can address the lack of exploration of the thermodynamics of QFT. The method was to compare the statistical moments of work and $\hat{\Delta U}$ (2.5) for unitary processes on quantum scalar fields. The moments had to be the same if the first law applied, because unitary processes do not exchange heat. We computed both the lowest moments and the distributions of work and $\hat{\Delta U}$.

We complete the description of the method by specifying the processes:

- Take a free scalar field on a (KMS) thermal state (both described in section 2.3).
- Apply a unitary operator generated by a modification of the Hamiltonian localized in spacetime.
- Suppress the modification to recover the free field.

Concretely, the unitary operator is generated by a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_{free} + \lambda \int_{\mathbb{R}} \mathrm{d}t\, \chi(t) \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{x}\, F(\boldsymbol{x}) \hat{O}(t, \boldsymbol{x}) \tag{3.1}$$

where $\hat{H}_{free}$ is the Hamiltonian of the free field, λ is a constant that regulates the strength of the process, $\chi(t)$ and $F(\boldsymbol{x})$ are switching and smearing functions, which specify an arbitrary time and space localization of the unitary in the lab frame. In general $\chi(t)$ will have a strong support on $[0, \tau]$, which implies that $\hat{H}_0 \approx \hat{H}_\tau \approx \hat{H}_{free}$, and $F(\boldsymbol{x})$ will have a strong support on a finite region of space. Finally, $\hat{O}$ is a field observable, which for a free field is always a linear combination of the quantum field amplitude $\hat{\phi}$ and its canonical momentum $\hat{\pi}$. We take $\hat{O} = \hat{\phi}$ to obtain simpler expressions, but we could also include $\hat{\pi}$ and calculations would remain similar.

The method just described can be used to further explore the thermodynamics of QFT (e.g. compute localization of work and to check the fluctuation theorems [8]). A suitable extension of the method could allow the computation of non-trivial ratios of free-energies for QFT via the fluctuation theorems, as also proposed in [8]. This is interesting because these ratios are remarkably difficult to compute for QFT when using path integrals. The extension is to end with a Hamiltonian different to $\hat{H}_{free}$. This would account for the processes that start on a free field, evolve it and leave it as an interacting field.

3.2 Requirements for Quantum Work Distributions

Work is meaningful as long as it satisfies some requirements. Some requirements are features that we would want in any work distribution (e.g., to be relatable to a classical definition of work, or to be associated to a protocol to measure work) and some others are tied to the relativistic nature of QFT. Concretely, we require a series of features from any work distribution, which are motivated by thermodynamics:

1. We want the work distribution to fulfill the fluctuation theorems, Crook's theorem [22] and Jarzynski equality [23]. These theorems are remarkable for relating work for arbitrary out-of-equilibrium processes with familiar equilibrium quantities. The classical definition of work satisfies them [22, 23, 41] and some of the quantum work distributions [5].

2. We want the work distribution to fulfill the first law of thermodynamics in average and in variance. For adiabatic processes this would read

$$\left\langle \Delta\hat{U}^k \right\rangle = \left\langle W^k \right\rangle \quad k = 1, 2. \tag{3.2}$$

   Quantum work distributions cannot satisfy the first law of thermodynamics for all the moments and at the same time satisfy the fluctuation theorems [5]. However, there are quantum work distributions that satisfy this relaxed version of the first law and the fluctuation theorems. The first law for the variances can be useful to study the size of the fluctuations, which play a big role in quantum thermodynamics [1, 2].

3. We need a protocol to measure the work distribution. Thermodynamics originated for practical purposes, in the same spirit work should be accessible through experimentation and relatable to a notion of useful energy.

The no-go theorem (see section 2.1.5) suggests that it is impossible to construct a probability work distribution that satisfies requirements 1 and 2 simultaneously. Indeed, the existing work proposals satisfying requirements 1 and 2 are not probability distributions [5]. Since these requirements are thermodynamics motivated and we want to keep them, we drop the assumption of having a probability work distribution. Instead, we take work to be a quasi-probability distribution. This is reasonable, because quasi-probabilities, such as the Wigner function, are successful in quantum mechanics (see section 2.2).

3.2.1 Extra Requirements for QFT Work Distributions

There are two extra requirements for any work distribution to be well-defined in a relativistic setting in the context of QFT:

4. The definition of the work distribution can not rely on projective measurements. The reason is that projective measurements are incompatible with the relativistic nature of QFT [9, 10, 11, 12, 8]. This excludes the most used work distribution, the two-point measurement scheme (TPM) [5]. Work distributions that do not rely on projective measurements can be built using probe-based protocols: the information about the work distribution gets imprinted on a probe through interaction with the system and then is extracted by projectively measuring the probe. Probe-based work distributions have been proposed in non-relativistic contexts [42, 43, 44, 45, 27, 28, 19] and were successfully adapted to the covariant formalism of QFT [8].

5. The work distribution shall be well-defined for processes involving thermal states. This is needed to have fluctuation theorems. However, this requirement is non-trivial for QFT because the usual notion of Gibbs thermality breaks down (for instance, the partition function of a field in free space diverges). This in turn breaks the existing proofs of the fluctuation theorems, which rely on Gibbs thermality [6]. The right notion of thermality is the more general KMS thermality. This requirement asks the work distribution to handle KMS states even when Gibbs states are ill-defined.

The complete list of requirements (both for any work distribution and specific for a QFT context) guided a search in the literature for meaningful work distributions in QFT, reducing the number of proposals of work distributions in non-relativistic settings that we had to explore in detail. We will show that three quasi-probability work distributions fulfill the requirements for all states (or a class of states that includes KMS states, for one of the distributions) in the coming section. Another benefit of the list was that some requirements were unknown for these distributions, which pointed to possible interesting results that lacked a proof.

Chapter 4

Results

4.1 Quasi-probability Work Distributions for QFT

We are going to expose proposals of work distributions that are useful for QFT. They are quasi-probability work distributions, which is expected because we searched for work distributions compatible with the requirements exposed in section 3.2. We discussed there how the requirements lead to quasi-probability work distributions.

Two quasi-probability work distributions meet all the requirements, which makes them meaningful notions of fluctuating work in QFT: the Allahvedyan-Terletsky-Margenau-Hill (ATMH) [26] and the Full-Counting Statistics (FCS) [27] work distributions. A third quasi-probabilty work distribution was recently proposed precisely in the context of QFT, the Ramsey scheme work distribution [8], which motivated the present research. This distribution has the advantage that the experimental protocol (requirement 3) can be associated to measurements with Unruh-DeWitt detectors [37, 38, 39], which are good models for measurements of quantum fields and can be connected with the interaction of atomic probes with the quantum electromagnetic field [46]. Moreover, the Ramsey scheme work distribution fulfills all the requirements except for satisfying the first law in variance (requirement 2), which it does satisfy for a class of states including the KMS thermal states (the exact class of states is in 4.1.5). Interestingly, the real part of the Ramsey scheme work distribution fulfills all the requirements and in fact is the ATMH work distribution. This implies that, while the previous protocol to measure the ATMH work distribution required projective measurements [36, 5], it is possible to measure the ATMH distribution without projective measurements on the system, as required to be compatible with QFT (requirement 4). We will show this relation in what follows and detail how each work distribution satisfies the requirements.

4.1.1 Ramsey Scheme Work Distribution

This work distribution was introduced in [8] as a generalization (to the covariant QFT setting) of the Ramsey scheme protocol to measure the TPM distribution in non-relativistic scenarios devised in [42, 43]. Concretely, the Ramsey scheme work distribution (P_{RS}) is the inverse Fourier transform of the characteristic function

$$\widetilde{P}_{\text{RS}}(\mu) = \left\langle \hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}e^{-\mathrm{i}\mu\hat{H}_0}\right\rangle_{\hat{\rho}}, \tag{4.1}$$

$$P_{\text{RS}}(W) = \mathcal{F}^{-1}\{\widetilde{P}_{\text{RS}}\}(W) = \frac{1}{2\pi}\int \widetilde{P}_{\text{RS}}(\mu)e^{-\mathrm{i}W\mu}\mathrm{d}\mu\,. \tag{4.2}$$

Where $\hat{\rho}$ is the state of the system at the start of the unitary process whose work we are assessing, $\hat{U}$ is the unitary operator applied during the process, $\hat{H}_0$ the system Hamiltonian at the start of the process and $\hat{H}_\tau$ the system Hamiltonian at the end of the process. This characteristic function coincides with the characteristic function of TPM [4, 19] when it is well-defined and $[\hat{\rho}, \hat{H}_0] = 0$ (i.e. the state is diagonal in the eigenbasis of the system's initial Hamiltonian). We go beyond both situations but P_{RS} remains well-defined, as a quasi-probability distribution, as we see in Appendix A.1. Interestingly, the real part of P_{RS} is the ATMH work distribution, as we will see below.

We proceed to specify the protocol that yields the Ramsey scheme distribution [42, 43]:

- Take a system in the state $\hat{\rho}$, together with a qubit that will serve as a probe $\hat{\rho}\otimes|0\rangle\langle 0|$.

- Apply the Hadamard gate on the qubit to obtain $\hat{\rho}\otimes|+\rangle\langle +|$.

- Apply the controlled unitary evolution:

$$\hat{M}_\mu = \hat{U} e^{-\mathrm{i}\mu \hat{H}_0} \otimes |0\rangle\langle 0| + e^{-\mathrm{i}\mu \hat{H}_\tau} \hat{U} \otimes |1\rangle\langle 1|. \tag{4.3}$$

- Apply a second Hadamard to the qubit.

- Determine the reduced state of the qubit after the previous steps, for instance with quantum state tomography.

The reduced state of the qubit is $\hat{\rho}_\mu = \frac{1}{2}[\mathbb{I} + \mathrm{Re}(\widetilde{P}_{\mathrm{RS}}(\mu))\hat{\sigma}_z + \mathrm{Im}(\widetilde{P}_{\mathrm{RS}}(\mu))\hat{\sigma}_y]$ at the end of the protocol, which allows the experimenter to recover the work distribution P_{RS} without projective measurements on the system. This accounts for the Ramsey scheme work distribution following requirements 3 (measurement protocol) and 4 (no projective measurements). Moreover, the Ramsey scheme protocol is easily implementable in scenarios where probes can couple to the system, including QFT using particle-detectors. The interferometric techniques proposed to implement the protocol [42, 43] are so suited to experimentation that the protocol was implemented in an NMR setting a year after [47]. In comparison, there are few experimental realizations of work distributions [48, 49, 50, 51] and they focus on the TPM distribution, except for [51].

The Ramsey scheme work distribution also satisfies requirement 5 (thermal states). It can handle KMS thermal states, because the work distribution can be expressed in terms of the field's Wightman n-point functions [8], which in turn can be easily evaluated for KMS states [40].

The remaining requirements 1 (fluctuation theorems) and 2 (first law of thermodynamics) will be discussed for all distributions together at the end.

4.1.2 Allahvedyan-Terletsky-Margenau-Hill Work Distribution

The ATMH work distribution (P_{ATMH}) was introduced in [26]. It is tied to the Terletsky-Margenau-Hill joint quasi-probability distribution of non-commuting observables [30, 31] particularized to the internal energy at the start ($\hat{H}_0$) and at the end ($\hat{U}^\dagger \hat{H}_\tau \hat{U}$) of the unitary process,

$$p_{\text{TMH}}(i,j) = \operatorname{Re}\left\langle \hat{U}^\dagger |\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}|\epsilon_i\rangle\langle\epsilon_i| \right\rangle_{\hat{\rho}}, \tag{4.4}$$

$$P_{\text{ATMH}}(W) = \sum_{ij} p_{\text{TMH}}(i,j)\,\delta\big(W - (\epsilon'_j - \epsilon_i)\big). \tag{4.5}$$

Where $\{|\epsilon_i\rangle\}$ and $\{|\epsilon'_j\rangle\}$ are the eigenbasis of $\hat{H}_0$ and $\hat{H}_\tau$ respectively. This expression is problematic for QFT because it involves rank one projectors and might contradict the requirement 4 (no projective measurements). Opportunely, the problem disappears for the ATMH characteristic function, which we obtain Fourier transforming (4.5),

$$\begin{aligned}\widetilde{P}_{\text{ATMH}}(\mu) &= \sum_{i,j} e^{\mathrm{i}\mu(\epsilon'_j-\epsilon_i)} \operatorname{Re}\left\langle \hat{U}^\dagger|\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}|\epsilon_i\rangle\langle\epsilon_i|\right\rangle_{\hat{\rho}} \\ &= \frac{1}{2}\left\langle \hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}e^{-\mathrm{i}\mu\hat{H}_0} + e^{-\mathrm{i}\mu\hat{H}_0}\hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}\right\rangle_{\hat{\rho}}.\end{aligned} \tag{4.6}$$

The ATMH work distribution can be obtained from a protocol as a weak measurement [36, 5], but it requires projective measurements, which would contravene requirement 4. However, there is an alternative thanks to $P_{\text{ATMH}} = \operatorname{Re}\{P_{\text{RS}}\}$. First, we see this equality comparing (4.1) and (4.6) to obtain $\widetilde{P}_{\text{ATMH}}(\mu) = \frac{1}{2}\big(\widetilde{P}_{\text{RS}}(\mu) + \widetilde{P}_{\text{RS}}(-\mu)^*\big)$, where * indicates the complex conjugation. Since $\mathcal{F}\{(P_{\text{RS}})^*\}(\mu) = \widetilde{P}_{\text{RS}}(-\mu)^*$, then $P_{\text{ATMH}} = \operatorname{Re}\{P_{\text{RS}}\}$. As a consequence, the ATMH distribution satisfies requirements 3 (measurement protocol) and 4: we can measure it with the probe-based protocol that defines P_{RS}.

The ATMH distribution satisfies requirement 5 (thermal states), which the Ramsey scheme work distribution satisfies, because for thermal states $P_{\text{RS}} = P_{\text{ATMH}}$. We verify this equality comparing the characteristic functions (4.1) and (4.6) to see $[\hat{\rho}, \hat{H}_0] = 0 \Rightarrow P_{\text{RS}} = P_{\text{ATMH}}$ and knowing that KMS thermal states commute with $\hat{H}_0$. There are more states where $P_{\text{RS}} = P_{\text{ATMH}}$ is true and we relate them to the fulfillment of requirement 2 (first law of thermodynamics) for P_{RS} in the section 4.1.5.

4.1.3 Full-Counting Statistics Work Distribution

The FCS work distribution was introduced in [27] and can be seen as the FCS distribution [32, 33, 34] of the internal energy change produced by a unitary process. The article [5] points out that this distribution is rooted in the Kyeldish formalism. It is an instance of the formalism assigning a joint distribution to non-commuting observables [35]. The FCS characteristic function of work is

$$\widetilde{P}_{\text{FCS}}(\mu) = \left\langle e^{-\mathrm{i}\frac{\mu}{2}\hat{H}_0}\hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}e^{-\mathrm{i}\frac{\mu}{2}\hat{H}_0}\right\rangle_{\hat{\rho}}, \tag{4.7}$$

which naturally arises as a phase-shift between two distinguishable states of a detector [27]. This leads to a proposal to measure P_{FCS} without projective measurements on the system [28], fulfilling requirements 3 (measurement protocol) and 4 (no projective measurements). The FCS distribution satisfies requirement 5 (thermal states), which the Ramsey scheme work distribution satisfies, because for thermal states $P_{\text{RS}} = P_{\text{ATMH}} = P_{\text{FCS}}$. We see this comparing (4.1), (4.6) and (4.7) to get

$$[\hat{\rho}, \hat{H}_0] = 0 \Rightarrow P_{\text{RS}} = P_{\text{ATMH}} = P_{\text{FCS}} \tag{4.8}$$

and knowing KMS states commute with $\hat{H}_0$.

Interestingly, the FCS work distribution might be able to assess the work performed by arbitrary processes (not necessarily adiabatic), through an extension to open systems proposed in the same article that introduced it [27].

4.1.4 Fluctuation Theorems on KMS states

We now show that the three work distributions, Ramsey Scheme, ATMH and FCS, can fulfill requirement 1 (fluctuation theorems). The work fluctuation theorems, Crooks theorem [22] and Jarzynski equality [23], only regard thermal states $\hat{\rho}_\beta$ of the system Hamiltonian at the start of the process $\hat{H}_0$, were β indicates the inverse temperature. For thermal states, we have $P_{\text{RS}} = P_{\text{ATMH}} = P_{\text{FCS}}$ as a consequence of (4.8) and $\left[\hat{\rho}_\beta, \hat{H}_0\right] = 0$. Therefore, we can prove the fluctuation theorems for the three distributions at once, for concreteness we choose to use the characteristic function $\widetilde{P} \equiv \widetilde{P}_{\rm RS}$ at (4.1).

The three distributions do satisfy fluctuation theorems for systems where TPM scheme and Gibbs thermal states are well-defined. The reason is that $\widetilde{P}$ coincides with the TPM characteristic function for thermal states [4] and TPM is the first quantum work distribution to which fluctuation theorems were exported [6, 5]. However stopping here would contravene the requirements 4 (no projective measurements) and 5 (thermal states), leaving open the possibility that the work distributions are ill-defined in the context of QFT. We shall instead use the characteristic function and KMS thermality to prove the fluctuation theorems.

Crooks theorem [22] relates P for a unitary process $\hat{U}$ and an initial KMS state of $\hat{H}_0$ with the work distribution of the time-reversed process (P_{rev}) implemented by $\hat{U}^\dagger$ on a KMS state of $\hat{H}_\tau$, and where at the end of the process the Hamiltonian is $\hat{H}_0$. Crooks theorem states [18, 24, 52]

$$\frac{P(W)}{P_{rev}(-W)} = e^{\beta(W-\Delta F)} \Leftrightarrow \frac{\widetilde{P}(\mu+\mathrm{i}\beta)}{\widetilde{P}_{rev}(-\mu)} = e^{-\beta\Delta F}. \tag{4.9}$$

Here ΔF is the change in free energy, and for general KMS states it is defined as $\Delta F = \frac{1}{\beta}\ln\langle e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\rangle_{\hat{\rho}_\beta}$. When Gibbs states are well defined we recover $\langle e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\rangle_{\hat{\rho}_\beta} = \operatorname{Tr} e^{-\beta\hat{H}_\tau}/\operatorname{Tr} e^{-\beta\hat{H}_0}$, i.e., the ratio of the partition functions of thermal states in the final and initial Hamiltonian. The proof of Crook's theorem simplifies when $\hat{H}_\tau = \hat{H}_0$, i.e. the process is cyclic. Then $\Delta F = 0$ and we should find $\widetilde{P}(\mu+\mathrm{i}\beta) = \widetilde{P}_{rev}(-\mu)$. We obtain this applying the 2) KMS condition (section 2.3.3) on $\widetilde{P}(\mu+\mathrm{i}\beta)$,

$$\begin{aligned}\widetilde{P}(\mu+\mathrm{i}\beta) &= \left\langle \hat{U}^\dagger e^{\mathrm{i}(\mu+\mathrm{i}\beta)\hat{H}_0}\hat{U}e^{-\mathrm{i}(\mu+\mathrm{i}\beta)\hat{H}_0}\right\rangle_{\hat{\rho}_\beta} \\ &= \left\langle e^{\mathrm{i}\mu\hat{H}_0}\hat{U}e^{-\mathrm{i}\mu\hat{H}_0}\hat{U}^\dagger\right\rangle_{\hat{\rho}_\beta},\end{aligned} \tag{4.10}$$

which equals $\widetilde{P}_{rev}(-\mu)$ due to $\left[\hat{\rho}_\beta, \hat{H}_0\right] = 0$. This proves Crooks theorem for $\hat{H}_\tau = \hat{H}_0$, which in turn implies [18] Jarzynski equality [23],

$$\left\langle e^{-\beta W}\right\rangle_{\hat{\rho}_\beta} = e^{-\beta\Delta F}. \tag{4.11}$$

For the general case $\hat{H}_\tau \neq \hat{H}_0$ we have an incomplete proof, presented in the Appendix A.4. We lack to show that $e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\hat{\rho}_\beta$ is an unnormalized KMS state of $\hat{H}_\tau$. With this proof complete, the three work distributions would satisfy requirement 1, within the rules imposed by requirements 4 and 5, bringing the fluctuation theorems to the QFT setting.

4.1.5 The First Law of QFT Thermodynamics

Lastly, we explore the requirement 2 for the three work distributions and show that we have a first law of quantum thermodynamics, valid in the context of QFT. The law equates the first two moments of $\hat{\Delta U}$, as defined in (2.5), with the respective moments of W, which we compute from the characteristic function,

$$\left\langle W^k\right\rangle = \mathrm{i}^{-k}\,\frac{d^k}{d\mu^k}\widetilde{P}(\mu)\bigg|_{\mu=0}\,. \tag{4.12}$$

The Ramsey scheme work distribution fulfills

$$\left\langle\hat{\Delta U}\right\rangle = \langle W_{\text{RS}}\rangle\,, \tag{4.13}$$

$$\left\langle\hat{\Delta U}^2\right\rangle = \langle W_{\text{RS}}^2\rangle - \left\langle\left[\hat{U}^\dagger\hat{H}_\tau\hat{U},\hat{H}_0\right]\right\rangle\,, \tag{4.14}$$

as computed in Appendix A.2. Consequently, requirement 2 is fulfilled for states where $\left\langle\left[\hat{U}^\dagger\hat{H}_\tau\hat{U},\hat{H}_0\right]\right\rangle = 0$, which holds for states that commute with $\hat{H}_0$ and in particular for KMS thermal states. $\left\langle\left[\hat{U}^\dagger\hat{H}_\tau\hat{U},\hat{H}_0\right]\right\rangle$ is imaginary, because $\mathrm{Re}\{P_{\text{RS}}\} = P_{\text{ATMH}} \implies \mathrm{Re}\{\langle W_{\text{RS}}^2\rangle\} = \langle W_{\text{ATMH}}^2\rangle$ and the ATMH distribution follows the first law for the second moments, as exposed next. One may then consider that discarding the imaginary part is positive, but this is not as clear because $\mathrm{Im}\{P_{\text{RS}}\} \neq 0$ does not always cause a violation of the first law for the second moment, as we show in Appendix A.3

The ATMH and FCS work distributions fulfill requirement 2,

$$\left\langle W^k_{\text{ATMH}} \right\rangle = \left\langle \Delta \hat{U}^k \right\rangle = \left\langle W^k_{\text{FCS}} \right\rangle \,, \quad k = 1, 2 \tag{4.15}$$

identities given in [26] and [19], respectively.

The first law of thermodynamics is violated for the third and higher moments of the three work distributions. However, a deviation for the higher moments is necessary to satisfy requirement 1 (fluctuation theorems) [5]. Moreover, the deviation needs to appear even in the most classical-like scenario, initial thermal states, and indeed we find it for a free scalar field in section 4.2.2.

With this we conclude showing that the ATMH and FCS work distribution satisfy all the requirements, which provides us with a first law of thermodynamics valid in the context of QFT. Moreover, the Ramsey scheme satisfies them, excluding the first law of thermodynamics for the variances (part of requirement 2). There is also the necessity to complete the proof of the fluctuation theorems for arbitrary unitary processes, as discussed in section 4.1.4.

4.2 Work and Energy in Quantum Fields

We explored the first law of thermodynamics for quantum fields for the first time, following the method described in section 2.3.1. We provide non-perturbative expressions of the work and $\Delta \hat{U}$ distributions for initial KMS thermal states of a free scalar field which evolve under the Hamiltonian (3.1). The generated unitary operator is, setting $\hbar = 1$, using $\mathcal{T}$ as the time-ordering operator and in the Heisenberg image of the $\hat{H}_{free}$ Hamiltonian,

$$\hat{U} = \mathcal{T} e^{-\mathrm{i}\lambda \int \mathrm{d}t \chi(t) \int \mathrm{d}^3 \boldsymbol{x} \, F(\boldsymbol{x}) \hat{\phi}(t, \boldsymbol{x})} \,. \tag{4.16}$$

We can get rid of the time ordering by performing a Magnus expansion, which happens to be finite because of the fact that the commutators of the field operator are the identity,

$$\hat{U} = e^{\mathrm{i}\theta} e^{-\mathrm{i}\lambda \int \mathrm{d}t \chi(t) \int \mathrm{d}^3\boldsymbol{x}\, F(\boldsymbol{x}) \hat{\phi}(t,\boldsymbol{x})}, \tag{4.17}$$

with $e^{\mathrm{i}\theta}$ a complex phase that does not affect evolution. Remarkably, we can recognize the evolution as generated by the displacement operator $\hat{D}_\alpha$ with $\alpha(\boldsymbol{k}) = -\mathrm{i}\lambda \frac{\widetilde{\chi}(\omega_{\boldsymbol{k}})\widetilde{F}(\boldsymbol{k})^*}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}}$. The relative simplicity of this evolution allows to compute the work and $\Delta\hat{U}$ distributions non-perturbatively through Wick's theorem, the details of the calculation are in Appendix B.

4.2.1 Non-perturbative Work and Internal Energy Difference Distributions

We provide a single work distribution P, because the three work distributions that are meaningful in QFT and presented above coincide. They are the same because the process starts with a KMS state, a situation already encountered in section 4.1.4.

The characteristic function of work is

$$\widetilde{P}(\mu) = \exp\left[\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3\omega_{\boldsymbol{k}}} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{F}(\boldsymbol{k})|^2 \left(\mathrm{i}\sin\omega_{\boldsymbol{k}}\mu + \frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}(\cos\omega_{\boldsymbol{k}}\mu - 1)\right)\right] \tag{4.18}$$

as derived non-perturbatively in Appendix B.1. P is its inverse Fourier transform.

The internal energy difference distribution is a Gaussian with expectation

$$\left\langle \Delta\hat{U} \right\rangle_{\hat{\rho}_\beta} = \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{F}(\boldsymbol{k})|^2 \tag{4.19}$$

and variance

$$\left\langle \Delta\hat{U}^2 \right\rangle_{\hat{\rho}_\beta} - \left\langle \Delta\hat{U} \right\rangle_{\hat{\rho}_\beta}^2 = \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{F}(\boldsymbol{k})|^2 \omega_{\boldsymbol{k}} \frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}. \tag{4.20}$$

Remarkably these cumulants only contain powers of two of lambda, even though they are non-perturbative. We obtained the non-perturbative expression for the operator $\hat{\Delta U}$ as a step of the calculation of its distribution in Appendix B.2,

$$\hat{\Delta U} = -\lambda \int \mathrm{d}t \chi(t) \int \mathrm{d}^3\boldsymbol{x}\, F(\boldsymbol{x}) \dot{\hat{\phi}}(t, \boldsymbol{x}) + \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{F}(\boldsymbol{k})|^2 \mathbb{I}, \tag{4.21}$$

which can be applied to any state, not just KMS.

4.2.2 Higher Moments Violate the First Law of QFT Thermodynamics

The first law of thermodynamics would equate all the moments of the work and $\hat{\Delta U}$ distributions, because the process is adiabatic. For the $\hat{\Delta U}$ Gaussian distribution, all the moments are determined by the expectation and the variance. For the work we extract the moments from $\widetilde{P}$ in (4.18) through the formula for moments (4.12).

We see the first law in action in that the expectations and variances are the same, as per requirement 2. However, as discussed previously, there must be a deviation for higher moments, even for initial thermal states, because otherwise the work distributions would not follow requirement 1 (fluctuation theorems). Indeed, the higher moments deviate. This calculation tells us the deviation starts at the third moments

$$\langle W^3 \rangle - \left\langle \hat{\Delta U}^3 \right\rangle = \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{F}(\boldsymbol{k})|^2 \omega_{\boldsymbol{k}}^2 \tag{4.22}$$

and becomes more significant the higher the moment: $\left\langle \hat{\Delta U}^k \right\rangle \in \mathcal{O}\big(\lambda^k\big)$ while $\langle W^k \rangle$ always has terms of degree $i = 2, 4, \ldots, 2k$ on λ, which can be respectively seen from (4.21) and from computing $\langle W^k \rangle$ from $\widetilde{P}$. Moments up to the fourth are in the table of Appendix B.3. Remarkably, the deviations for the third and higher moments remain significant even for small strengths of the unitary operation λ: all the deviations have terms λ^2, which make them of the same order as the interesting quantities, the expectation and variance of work or $\hat{\Delta U}$ (cf. (4.19) and (4.20)).

4.2.3 Perturbative Calculation of Internal Energy Difference

There is an alternative way to compute the moments of $\Delta\hat{U}$ and work above, through the Dyson expansion of the unitary (4.16), which results in a perturbative calculation. The result should be the same, but it is non-trivial to show so. We will show that this is the case for the vacuum $|\Omega\rangle$ expectation of $\Delta\hat{U}$ computed perturbatively up to fourth degree in λ,

$$\begin{aligned}
&\left\langle \Delta\hat{U} \right\rangle_\Omega = \\
&\quad \lambda^2 \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3 2} |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 \left|\widetilde{F}(\boldsymbol{k})\right|^2 \\
&+ \lambda^4 \int\int \frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k'}}{(2\pi)^6 2^2} \left|\widetilde{F}(\boldsymbol{k})\right|^2 \left|\widetilde{F}(\boldsymbol{k'})\right|^2 \frac{\omega_{\boldsymbol{k}} + \omega_{\boldsymbol{k'}}}{\omega_{\boldsymbol{k}}\omega_{\boldsymbol{k'}}} \int \mathrm{d}t_1 \chi(t_1) \int^{t_1} \mathrm{d}t_2 \chi(t_2) \int \mathrm{d}t_3 \chi(t_3) \\
&\quad \times \int^{t_3} \mathrm{d}t_4 \chi(t_4) \left(e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1 - t_3) + \omega_{\boldsymbol{k'}}(t_2 - t_4)]} + e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1 - t_4) + \omega_{\boldsymbol{k'}}(t_2 - t_3)]} \right) \\
&- \lambda^4 \int\int \frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k'}}{(2\pi)^6 2^2} \left|\widetilde{F}(\boldsymbol{k})\right|^2 \left|\widetilde{F}(\boldsymbol{k'})\right|^2 \frac{1}{\omega_{\boldsymbol{k}}} \int \mathrm{d}t_1 \chi(t_1) \int^{t_1} \mathrm{d}t_2 \chi(t_2) \int^{t_2} \mathrm{d}t_3 \chi(t_3) \int \mathrm{d}t_4 \chi(t_4) \\
&\quad \times 2\,\mathrm{Re}\left\{ e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1 - t_3) + \omega_{\boldsymbol{k'}}(t_2 - t_4)]} + e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_2 - t_3) + \omega_{\boldsymbol{k'}}(t_1 - t_4)]} + e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1 - t_2) + \omega_{\boldsymbol{k'}}(t_3 - t_4)]} \right\} \\
&+ \mathcal{O}\left(\lambda^6\right)
\end{aligned} \tag{4.23}$$

as obtained in Appendix B.4. The non-perturbative calculation of $\left\langle \Delta\hat{U} \right\rangle_\Omega$, (4.19) considering vacuum as a thermal state of $\beta \to \infty$, tells us that the fourth degree on λ should not exist (neither the higher degrees) and that they agree for the term of second degree on λ. The degree four on λ does seem to exist in the perturbative expression. However, the two appearing four degree terms can be simplified to get rid of the nested integrals and become the same but with opposite sign. The positive term simplification comes from

$$\int \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 + \int \mathrm{d}t_2 \int^{t_2} \mathrm{d}t_1 = \int \mathrm{d}t_1 \int \mathrm{d}t_2 \tag{4.24}$$

and the observation that the variables t_2 and t_1, $\omega_{\boldsymbol{k}}$ and $\omega_{\boldsymbol{k'}}$ can be exchanged without changing the value of the integral. The variables t_3 and t_4 can also be exchanged and the same argument applies, fully removing the nested integrals. Then, the term evaluates to

$$\lambda^4 \int\int \frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k}'}{(2\pi)^6 2^2} \left|\widetilde{F}(\boldsymbol{k})\right|^2 \left|\widetilde{F}(\boldsymbol{k}')\right|^2 |\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2 |\widetilde{\chi}(\omega_{\boldsymbol{k}'})|^2 \frac{1}{\omega_{\boldsymbol{k}}}. \tag{4.25}$$

The negative term evaluates to the opposite value following a similar argument, but permuting t_2, t_3 and t_4. This cancels the fourth degree and keeps consistency with the non-perturbative calculation. Finally, we did not check the cancellation of higher order terms but they must also cancel for the calculations to remain consistent.

Chapter 5

Discussion and Conclusions

5.1 Discussion

The truth of the first law of thermodynamics in QFT is dependant on the notion of fluctuating work chosen. Nevertheless, we showed that there are well-defined notions of work for unitary processes in QFT that fulfill the first law for the averages and the variances. This notion of fluctuating work is difficult to characterize already for quantum thermodynamics because it does not correspond to an observable on the system [53] and its no-go theorem [17] suggests that it is impossible to keep all the features of the classical work distribution. Moreover, the difficulty increases for QFT, because both projective measurements and Gibbs thermality are ill-defined, and previous notions of work fluctuations depended on them, with the TPM scheme work distribution as main example.

We dealt with the no-go theorem keeping the two requirements that are motivated by thermodynamics: 1) the fluctuation theorems 2) the first law of thermodynamics for averages (and moreover, for variances). We compiled all the requirements for work distributions in a list, allowing to see that there are work distributions meaningful in QFT, which are quasi-probabilities (Ramsey scheme, ATMH and FCS work distributions) and the same list could be a guide to find more. Interestingly, quasi-probabilities relate to other branches of quantum mechanics, the assignment of joint distributions to non-commuting observables (such as the Wigner function) and the characterization of contextuality, which can be done with the ATMH work distribution [36].

In this research the characteristic functions were the principal tool to define the work distributions and extract results about them. For the three work distributions explored the characteristic functions are well suited for QFT, because their expressions can be readily translated to the well defined n-point Wightmann functions of QFT [8], at least for KMS states. These functions are the base for the axiomatic algebraic QFT, which has the purpose to give solid foundations to QFT.

The Ramsey scheme interferometric protocol [42, 43] can experimentally be used to measure the effects of coherence on the initial energy basis for work, besides the purpose of measuring the TPM distribution. And both for the ATMH and Ramsey scheme work distributions. In particular, the depicted first law of thermodynamics allows experimental determination of the first two moments of $\hat{\Delta U}$. A measurement of which might not be possible otherwise, specially on settings where projective measurements are not possible, QFT among them.

The completion of the proof given for the fluctuating theorems for arbitrary unitary processes on QFT (not just cyclic) would allow to compute ratios of partition functions in QFT (i.e. free energy differences), this was pointed out by [8], and is remarkable because computing them with the present technique of path integrals is renowned to be difficult. Finally, the non-perturbative expression of the characteristic function of work for KMS states in a free scalar field opens the door to use it to analyze the exact thermodynamics of arbitrary unitary processes on this QFT scenario.

5.2 Conclusions

We conclude going through the details of the contributions of this thesis. We gave answers to the two objectives:

1. We provided the first instance of the first law of thermodynamics in a relativistic setting in the context of QFT. This is remarkable because it translates directly to one of the two fundamental theories of modern physics, the Standard Model, build

over QFT. Concretely, we showed the first law applies to the averages and variances of well-defined notions of fluctuating work for arbitrary unitary processes of QFT.

2. We showed that two existing quasi-probability work distributions, ATMH and FCS, are meaningful in the context of QFT, as they satisfy the list of requirements for work distributions of unitary processes that we constructed. We proved ATMH can be measured with the same interferometric protocol as Ramsey scheme work, protocol already implemented as an experiment and compatible with QFT, which were not features of the previous protocol to measure ATMH [36].

Moreover, the Ramsey scheme work distribution, which was already presented QFT, fulfills the first law of thermodynamics on average, and for the variance for a class of states which includes thermal states.

Regarding the work fluctuation theorems in QFT, we proved them for cyclic unitary processes, for the Ramsey scheme, ATMH and FCS work distributions. We proved them using the general KMS thermality, to be compatible with QFT, instead of using the ill-defined Gibbs thermality. We thus extended their reach in QFT beyond the cases for free scalar fields studied in [8]. We also provide a proof that lacks completion but that could prove the fluctuation theorems for arbitrary unitary processes.

The exploration of the first law of thermodynamics on a free scalar quantum field provided the non-perturbative expression for the work distribution of a general family of unitary processes applied to thermal states. It also allowed to see deviations to the first law of thermodynamics for the third and higher moments of W and $\hat{\Delta U}$, which can be of the same order as the average and variance of work, even when the evolution is arbitrarily weak.

5.2.1 Personal experience

To finish, my experience with this project has been really satisfactory. I liked that the topic I was proposed to work was rather new in the group of research, so we could learn about it with the supervisor. Most importantly, this Bachelor's final degree project sparked my curiosity for quantum thermodynamics, which was unknown for me before.

It has been a really good experience to take part on the process of writing the obtained results as an scientific article for publication.

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Appendix A

Properties of the work distributions

A.1 Proof that Ramsey scheme work is a quasi-probability distribution

We consider P_{RS}, as defined in (4.2), to be a quasi-probability because it follows $\int P_{\text{RS}}(W)\mathrm{d}W = 1$ and linearity under mixtures of $\hat{\rho}$, as we prove now. First, since $\widetilde{P}_{\text{RS}}$ is the Fourier transform of P_{RS},

$$\int P_{\text{RS}}(W)\mathrm{d}W = \widetilde{P}_{\text{RS}}(0) = \langle \mathbb{I} \rangle = 1\,. \tag{A.1}$$

To evaluate the Ramsey characteristic function of work see (4.1). P_{RS} is linear under mixtures of $\hat{\rho}$, because its Fourier transform $\widetilde{P}_{\text{RS}}$ is linear under mixtures of $\hat{\rho}$ by definition (it is an expected value). To round up, it is not a probability distribution, it indeed takes complex values, example. The initial state was not diagonal, as necessary.

A.2 The first law of thermodynamics in the Ramsey scheme work distribution

Here we compute the first two moments of Ramsey scheme work and compare them with the moments of energy difference. When they are equal we can say that we have a version of the first law. The heat does not appear on the first law because the evolution is unitary.

We compute the moments of the Ramsey scheme work from its characteristic function [43, 42],

$$\widetilde{P}(\mu) = \left\langle \hat{U}^\dagger e^{\mathrm{i}\mu \hat{H}_\tau} \hat{U} e^{-\mathrm{i}\mu \hat{H}_0} \right\rangle , \tag{A.2}$$

with $\langle W^k \rangle = \mathrm{i}^{-k} \, \frac{d^k}{d\mu^k} \widetilde{P}(\mu)\Big|_{\mu=0}$,

$$\begin{aligned} \langle W \rangle &= \left\langle \hat{U}^\dagger \hat{H}_\tau \hat{U} - \hat{H}_0 \right\rangle \\ \langle W^2 \rangle &= \left\langle \hat{U}^\dagger \hat{H}_\tau^2 \hat{U} - 2\hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0 + \hat{H}_0^2 \right\rangle . \end{aligned} \tag{A.3}$$

The energy difference operator or operator of work [5] is defined as

$$\Delta\hat{U} = \hat{U}^\dagger \hat{H}_\tau \hat{U} - \hat{H}_0 \, . \tag{A.4}$$

Then $\langle W \rangle = \left\langle \Delta\hat{U} \right\rangle$, the fist law holds in average. For the second moment

$$\left\langle \Delta\hat{U}^2 \right\rangle = \left\langle \hat{U}^\dagger \hat{H}_\tau^2 \hat{U} - \hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0 - \hat{H}_0 \hat{U}^\dagger \hat{H}_\tau \hat{U} + \hat{H}_0^2 \right\rangle . \tag{A.5}$$

The difference is

$$\langle W^2 \rangle - \left\langle \Delta\hat{U}^2 \right\rangle = \left\langle \left[\hat{U}^\dagger \hat{H}_\tau \hat{U}, \hat{H}_0 \right] \right\rangle , \tag{A.6}$$

the first law holds for the variances exactly when this difference amounts to zero. This includes initial KMS states and states that $\left[\hat{H}_0, \hat{\rho}\right] = 0$ or $\left[\hat{U}^\dagger \hat{U}, \hat{\rho}\right] = 0$. This is shown by expressing the difference as a trace and apply the cyclic property.

For 3rd or higher moments the first law fails. Even for initial thermal states, as seen in the table of Appendix B.3.

A.3 Relation between Ramsey scheme and ATMH distributions

The ATHM work distribution is the real part of the Ramsey scheme work distribution, $P_{\text{ATMH}} = \mathrm{Re}[P_{\text{RS}}]$, as was deduced in the main text from the expressions for the characteristic functions (4.1), (4.6). We might think that removing the imaginary part of the Ramsey scheme is positive: we gain that the first law is always true for the variance of the ATMH work distribution, while it is sometimes was false for the variance of the Ramsey scheme work distribution. However, the removal is not clearly positive, because the imaginary part might have information about the state and it does not always cause a violation of the first law for the variance. We prove the latter now. It suffices to provide an example process where $P_{\text{ATMH}} \neq P_{\text{RS}}$ and $\langle W_{\text{RS}}^2 \rangle = \left\langle \Delta\hat{U}^2 \right\rangle$. The simplest example is on a three-level system, because for two-level systems $\langle W_{\text{RS}}^2 \rangle = \left\langle \Delta\hat{U}^2 \right\rangle \implies P_{\text{ATMH}} = P_{\text{RS}}$ (see Appendix). Consider an initial state $\hat{\rho} = \frac{(|0\rangle + \mathrm{i}|1\rangle)(\langle 0| - \mathrm{i}\langle 1|)}{2}$, the process starts with Hamiltonian $\hat{H}_0 = |1\rangle\langle 1|$ and ends up with $\hat{H}_\tau = |0\rangle\langle 0| + 2|1\rangle\langle 1|$. The unitary evolution operator is $\hat{U} = \sum_{j=0}^{2} |j\rangle\langle \omega^j|$, where

$$\left|\omega^j\right\rangle = \frac{1}{\sqrt{3}}\big(|0\rangle + \omega^j\,|1\rangle + \omega^{2j}\,|2\rangle\big),\ j = 0,1,2. \tag{A.7}$$

Where $\omega = e^{\mathrm{i}\frac{2}{3}\pi}$ The $|\omega^j\rangle$ form an orthonormal basis, which ensures that $\hat{U}$ is unitary (it is a change of orthonormal basis). We will find that $\langle W_{\text{RS}}^2 \rangle - \left\langle \Delta\hat{U}^2 \right\rangle = \left\langle \left[\hat{U}^\dagger \hat{H}_\tau \hat{U}, \hat{H}_0\right] \right\rangle$ (equality from Appendix) is zero.

$$\left\langle \left[\hat{U}^\dagger \hat{H}_\tau \hat{U}, \hat{H}_0\right] \right\rangle = \left\langle \hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0 \right\rangle - \left\langle \left(\hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0\right)^\dagger \right\rangle = 2\mathrm{i}\,\mathrm{Im}\left\langle \hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0 \right\rangle, \tag{A.8}$$

because $\hat{U}^\dagger \hat{H}_\tau \hat{U}$ and $\hat{H}_0$ are Hermitian.

$$\begin{aligned}\left\langle \hat{U}^\dagger \hat{H}_\tau \hat{U} \hat{H}_0 \right\rangle &= \big\langle \big(|\omega^0\rangle\langle\omega^0| + 2|\omega^1\rangle\langle\omega^1|\big)|1\rangle\langle 1| \big\rangle \\ &= \frac{1}{2\sqrt{3}}(\langle 0| - \mathrm{i}\,\langle 1|)\big(|\omega^0\rangle\langle 1| + 2\omega^2|\omega^1\rangle\langle 1|\big)(|0\rangle + \mathrm{i}\,|1\rangle) \\ &= \frac{\mathrm{i}}{6}(1 + 2\omega^2 - 3\mathrm{i}) = \frac{1}{6}(\sqrt{3} + 3)\end{aligned} \tag{A.9}$$

Its imaginary part is zero, which means $\left\langle \left[\hat{U}^\dagger \hat{H}_\tau \hat{U}, \hat{H}_0\right] \right\rangle$ is zero and consequently $\langle W_{\text{RS}}^2 \rangle = \left\langle \Delta\hat{U}^2 \right\rangle$. We are left to find that $P_{\text{RS}} \neq P_{\text{ATMH}}$. Equivalently, we can prove that their characteristic functions differ,

$$
\begin{aligned}
\widetilde{P}_{\text{RS}}(\mu) - \widetilde{P}_{\text{ATMH}}(\mu) &= \frac{1}{2}\left\langle \hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}e^{-\mathrm{i}\mu\hat{H}_0} - e^{-\mathrm{i}\mu\hat{H}_0}\hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau}\hat{U}\right\rangle \\
&= \frac{1}{2}\left\langle e^{-\mathrm{i}\mu}\big(|\omega^0\rangle\langle 1| - |1\rangle\langle\omega^0|\big) + 2e^{\mathrm{i}\mu}\big(\omega^2|\omega^1\rangle\langle 1| - \omega|1\rangle\langle\omega^1|\big)\right\rangle \\
&= \frac{\mathrm{i}}{6}\big(e^{-\mathrm{i}\mu} - e^{\mathrm{i}\mu}\big).
\end{aligned} \tag{A.10}
$$

This difference will make $P_{\text{RS}} \neq P_{\text{ATMH}}$, by inducing two imaginary delta terms on the P_{RS} work distribution. Therefore the example process fulfills the two properties that we asked it. In turn, the imaginary terms on P_{RS} do not necessarily cause a violation of the first law for the second moment.

Sufficient conditions to get $P_{\text{RS}} = P_{\text{ATMH}}$:

$$
v \implies P_{\text{RS}} = P_{\text{ATMH}} \tag{A.11}
$$

Which comes from

$$
\widetilde{P}_{\text{RS}}(\mu) - \widetilde{P}_{\text{ATMH}}(\mu) = \frac{1}{2}\sum_{n,m}\frac{(\mathrm{i}\mu)^{n+m}}{n!m!}(-1)^m\left\langle\left[(\hat{U}^\dagger\hat{H}_\tau\hat{U})^n, \hat{H}_0^m\right]\right\rangle, \tag{A.12}
$$

consequence of $e^{\hat{A}} = \sum_n \frac{1}{n!}\hat{A}^n$. The distributions coincide when the condition in (A.11) is fulfilled because it is sufficient to make their characteristic functions equal.

Another sufficient condition, that works for systems with discrete energy levels, is

$$
\left\langle\left[\hat{U}^\dagger|\epsilon_j'\rangle\langle\epsilon_j'|\hat{U}, |\epsilon_i\rangle\langle\epsilon_i|\right]\right\rangle = 0 \quad \forall i,j \implies P_{\text{RS}} = P_{\text{ATMH}}, \tag{A.13}
$$

where $\{|\epsilon_i\rangle\}$ is the eigenbasis for the initial Hamiltonian $\hat{H}_0$ and $\{|\epsilon_j'\rangle\}$ the eigenbasis for the final Hamiltonian $\hat{H}_\tau$. This implication comes from the expressions of the distributions,

$$
P_{\text{ATMH}}(W) = \sum_{i,j}\mathrm{Re}\left\langle\hat{U}^\dagger|\epsilon_j'\rangle\langle\epsilon_j'|\hat{U}|\epsilon_i\rangle\langle\epsilon_i|\right\rangle\delta(W - (\epsilon_j' - \epsilon_i)), \tag{A.14}
$$

$$
P_{\text{RS}}(W) = \sum_{i,j}\left\langle\hat{U}^\dagger|\epsilon_j'\rangle\langle\epsilon_j'|\hat{U}|\epsilon_i\rangle\langle\epsilon_i|\right\rangle\delta(W - (\epsilon_j' - \epsilon_i)), \tag{A.15}
$$

which are equal when $\left\langle\left[\hat{U}^\dagger|\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}, |\epsilon_i\rangle\langle\epsilon_i|\right]\right\rangle = 0$ because then $\left\langle\hat{U}^\dagger|\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}|\epsilon_i\rangle\langle\epsilon_i|\right\rangle =$ Re $\left\langle\hat{U}^\dagger|\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}|\epsilon_i\rangle\langle\epsilon_i|\right\rangle$. This condition can be mechanically verified for finite-level systems and implies the previous one,

$$\left\langle\left[\hat{U}^\dagger|\epsilon'_j\rangle\langle\epsilon'_j|\hat{U}, |\epsilon_i\rangle\langle\epsilon_i|\right]\right\rangle = 0 \quad \forall i,j \implies \left\langle\left[(\hat{U}^\dagger\hat{H}_\tau\hat{U})^n, \hat{H}_0^m\right]\right\rangle = 0 \quad \forall n,m \in \mathbb{N}. \tag{A.16}$$

This is seen by decomposing the Hamiltonians on their energy eigenbasis, for example, $\hat{H}_0^m = \sum_i \epsilon_i^m |\epsilon_i\rangle\langle\epsilon_i|$.

A.3.1 Discrepancies between Ramsey scheme and ATMH on two-level systems

We will prove that for two-level systems we cannot simultaneously have $\langle W_{\text{RS}}^2\rangle = \left\langle\Delta\hat{U}^2\right\rangle$ and $P_{\text{ATMH}} \neq P_{\text{RS}}$.We start from $\langle W_{\text{RS}}^2\rangle = \left\langle\Delta\hat{U}^2\right\rangle$, which from Appendix is equivalent to

$$\left\langle\left[\hat{U}^\dagger\hat{H}_\tau\hat{U}, \hat{H}_0\right]\right\rangle = 0. \tag{A.17}$$

We decompose the Hamiltonians into their energy eigenbasis and define for readability $\left|\epsilon_j^H\right\rangle := \hat{U}\left|\epsilon'_j\right\rangle$, to obtain

$$\sum_{i,j=0}^{2} \epsilon_i\epsilon'_j \left\langle\left[|\epsilon_j^H\rangle\langle\epsilon_j^H|, |\epsilon_i\rangle\langle\epsilon_i|\right]\right\rangle = 0. \tag{A.18}$$

These commutators do not have much freedom on the value that they take thanks to the system having two levels,

$$\left[|\epsilon_1^H\rangle\langle\epsilon_1^H|, |\epsilon_1\rangle\langle\epsilon_1|\right] = \left[\mathbb{I} - |\epsilon_0^H\rangle\langle\epsilon_0^H|, \mathbb{I} - |\epsilon_0\rangle\langle\epsilon_0|\right] = \left[|\epsilon_0^H\rangle\langle\epsilon_0^H|, |\epsilon_0\rangle\langle\epsilon_0|\right] \tag{A.19}$$

where we used that $\{|\epsilon_0\rangle, |\epsilon_1\rangle\}$ and $\{\left|\epsilon_0^H\right\rangle, \left|\epsilon_1^H\right\rangle\}$ are both basis. Similarly, $\left[|\epsilon_0^H\rangle\langle\epsilon_0^H|, |\epsilon_1\rangle\langle\epsilon_1|\right] = \left[|\epsilon_1^H\rangle\langle\epsilon_1^H|, |\epsilon_0\rangle\langle\epsilon_0|\right] = -\left[|\epsilon_0^H\rangle\langle\epsilon_0^H|, |\epsilon_0\rangle\langle\epsilon_0|\right]$. Therefore (A.18) becomes,

$$(\epsilon_1 - \epsilon_0)(\epsilon'_1 - \epsilon'_0)\left\langle\left[|\epsilon_0^H\rangle\langle\epsilon_0^H|, |\epsilon_0\rangle\langle\epsilon_0|\right]\right\rangle = 0. \tag{A.20}$$

We have three ways to fulfill this equality. First, if $(\epsilon_1 - \epsilon_0) = 0$ then $\hat{H}_0 = \mathbb{I}$. This implies $P_{\text{ATMH}} = P_{\text{RS}}$, because $\widetilde{P}_{\text{RS}}(\mu) = \widetilde{P}_{\text{ATMH}}(\mu) = \left\langle \hat{U}^\dagger e^{\mathrm{i}\mu \hat{H}_\tau} \hat{U} \right\rangle$. When $(\epsilon_1' - \epsilon_0') = 0$ we find an analogous situation and $P_{\text{ATMH}} = P_{\text{RS}}$. The last way is $\left\langle \left[|\epsilon_0^H\rangle\langle\epsilon_0^H|, |\epsilon_0\rangle\langle\epsilon_0| \right] \right\rangle = 0$ and also implies $P_{\text{ATMH}} = P_{\text{RS}}$, because from the previous equalities then $\left\langle \left[|\epsilon_i^H\rangle\langle\epsilon_i^H|, |\epsilon_j\rangle\langle\epsilon_j| \right] \right\rangle = 0$ which is the condition of (A.13). Therefore, there is no way to get $P_{\text{ATMH}} \neq P_{\text{RS}}$, as we wanted to prove. It is incompatible with having $\langle W_{\text{RS}}^2 \rangle = \left\langle \Delta\hat{U}^2 \right\rangle$ on a two level-system.

A.4 Fluctuation theorems

Our objective is to prove Crooks theorem, as stated in (4.9), for the three quasi-probability work definitions. Which we showed in the main text that they become one when restricted to KMS states, or in general to states $\left[\hat{\rho}, \hat{H}_0\right] = 0$. We prove Crooks for the three definitions of work by proving it for the unique definition on KMS states.

We proceed to give the start of a proof for the Crooks theorem for the most general situation of a unitary process $\hat{U}$ that starts with a Hamiltonian $\hat{H}_0$ and finishes with $\hat{H}_\tau$. The initial state will be KMS, KMS of $\hat{H}_0$ for the forward process and KMS of $\hat{H}_\tau$ for the reverse process. We denote them as $\hat{\rho}_\beta^0$ and $\hat{\rho}_\beta^\tau$ respectively, with β the inverse temperature. The Crooks theorem relates the functions

$$\widetilde{P}(\mu + \mathrm{i}\beta) = \left\langle \hat{U}^\dagger e^{\mathrm{i}(\mu+\mathrm{i}\beta)\hat{H}_\tau} \hat{U} e^{-\mathrm{i}(\mu+\mathrm{i}\beta)\hat{H}_0} \right\rangle_{\hat{\rho}_\beta^0} \qquad \widetilde{P}_{rev}(-\mu) = \left\langle \hat{U} e^{-\mathrm{i}\mu\hat{H}_0} \hat{U}^\dagger e^{\mathrm{i}\mu\hat{H}_\tau} \right\rangle_{\hat{\rho}_\beta^\tau}. \tag{A.21}$$

To prove the relation we will start at $\widetilde{P}(\mu + \mathrm{i}\beta)$ and using the KMS conditions we will reach $\widetilde{P}_{rev}(-\mu)$ times a constant. Let us introduce a new variable, μ', and a new function

$$\widetilde{P}'(\mu, \mu') = \left\langle \hat{U}^\dagger e^{\mathrm{i}\mu'\hat{H}_\tau} e^{-\mathrm{i}\mu'\hat{H}_0} e^{\mathrm{i}\mu\hat{H}_0} \hat{U} e^{-\mathrm{i}\mu\hat{H}_0} \right\rangle_{\hat{\rho}_\beta^0} \tag{A.22}$$

such that $\widetilde{P}'(\mu, \mu) = \widetilde{P}(\mu)$. Apply the KMS property $\langle B(t)A \rangle = \langle AB(t + \mathrm{i}\beta) \rangle$, where $B(t) = e^{\mathrm{i}t\hat{H}_0} B e^{-\mathrm{i}t\hat{H}_0}$ and both A and B are bounded operators, with μ as t, to get

$$\widetilde{P}'(\mu + \mathrm{i}\beta, \mu' + \mathrm{i}\beta) = \left\langle e^{\mathrm{i}\mu\hat{H}_0} \hat{U} e^{-\mathrm{i}\mu\hat{H}_0} \hat{U}^\dagger e^{\mathrm{i}(\mu'+\mathrm{i}\beta)\hat{H}_\tau} e^{-\mathrm{i}(\mu'+\mathrm{i}\beta)\hat{H}_0} \right\rangle_{\hat{\rho}_\beta^0} \tag{A.23}$$

We go back to the characteristic function by equating μ and μ',

$$\widetilde{P}(\mu+\mathrm{i}\beta)=\left\langle \hat{U}e^{-\mathrm{i}\mu\hat{H}_0}\hat{U}^{\dagger}e^{\mathrm{i}\mu\hat{H}_\tau}e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\right\rangle_{\hat{\rho}^0_\beta}, \tag{A.24}$$

also, we used $\left[\hat{\rho}^0_\beta,\hat{H}_0\right]=0$. If we prove that $e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\hat{\rho}^0_\beta$ is an unnormalized KMS thermal state of $\hat{H}_\tau$, then we get the Crooks theorem in the following form

$$\widetilde{P}(\mu+\mathrm{i}\beta)=\widetilde{P}_{rev}(-\mu)\,\mathrm{Tr}\left\{e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\hat{\rho}^0_\beta\right\}. \tag{A.25}$$

To get the original Crooks theorem we can define $e^{-\beta\Delta F}=\mathrm{Tr}\left\{e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\hat{\rho}^0_\beta\right\}$, which recovers the usual free energy definition on Gibbs states. It is left to prove that $e^{-\beta\hat{H}_\tau}e^{\beta\hat{H}_0}\hat{\rho}^0_\beta$ is an unnormalized KMS thermal state of $\hat{H}_\tau$.

Appendix B

Calculations for the thermodynamics on quantum free scalar fields

We will need to make use of the field operator:

$$\hat{\phi}(t, \boldsymbol{x}) = \int \frac{\mathrm{d}^3\boldsymbol{k}}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}}\left(e^{-\mathrm{ik}\cdot\mathrm{x}}\hat{a}^\dagger_{\boldsymbol{k}} + e^{\mathrm{ik}\cdot\mathrm{x}}\hat{a}_{\boldsymbol{k}}\right) \tag{B.1}$$

$$\mathsf{k}\cdot\mathsf{x} = \boldsymbol{k}\cdot\boldsymbol{x} - \omega_{\boldsymbol{k}}t\,, \quad \omega_{\boldsymbol{k}} = \sqrt{m^2 + |\boldsymbol{k}|^2} \tag{B.2}$$

Where m is the mass of the field and $\left[\hat{a}_{\boldsymbol{k}}, \hat{a}^\dagger_{\boldsymbol{k}'}\right] = \delta(\boldsymbol{k} - \boldsymbol{k}')\mathbb{I}$. These are not the full commutation relations For convenience, define:

$$\hat{\phi}_F(t) = \int \mathrm{d}^3\boldsymbol{x}F(\boldsymbol{x})\hat{\phi}(t, \boldsymbol{x}) \qquad \hat{\phi}_{\chi F} = \int \mathrm{d}t\chi(t)\hat{\phi}_F(t) \tag{B.3}$$

The unitary processes that we apply to the field is, setting $\hbar = 1$ and using $\mathcal{T}$ as the time-ordering operator,

$$\hat{U} = \mathcal{T}e^{-\mathrm{i}\lambda\hat{\phi}_{\chi F}}\,. \tag{B.4}$$

Without simplification this would require us to perform an infinite series of nested time integrals. However, we get a finite series performing the Magnus expansion. This is thanks to $\left[\hat{\phi}_F(t), \hat{\phi}_F(t')\right] \propto \mathbb{I}$, which causes further commutators with $\hat{\phi}_F$ to vanish. The consequence is that we obtain the closed-form for the family of unitaries

$$\hat{U} = e^{\mathrm{i}\theta} e^{-\mathrm{i}\lambda\hat{\phi}_{\chi F}}, \tag{B.5}$$

with θ a real phase. They are a displacement, up to the phase.

We now prove θ is a real phase and that $\left[\hat{\phi}_F(t), \hat{\phi}_F(t')\right] \propto \mathbb{I}$ at the same time. The expression for θ is

$$\theta = i\lambda^2 \int \mathrm{d}t \int^t \mathrm{d}t' \chi(t)\chi(t') \left\langle \left[\hat{\phi}_F(t), \hat{\phi}_F(t')\right] \right\rangle . \tag{B.6}$$

Where the expectation is just used to remove the identity operator. We have to compute the commutator. To ease calculation, split the field operators

$$\hat{\phi}_F(t) = \hat{\phi}_F^+(t) + \hat{\phi}_F^-(t) \qquad \hat{\phi}_F^+(t) = \int \frac{\mathrm{d}^3\boldsymbol{k}}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}} \widetilde{F}(\boldsymbol{k})^* e^{\mathrm{i}\omega_{\boldsymbol{k}} t} \hat{a}_{\boldsymbol{k}}^\dagger \tag{B.7}$$

The commutator will split in four terms, as an example we calculate $\left[\hat{\phi}_F^+(t), \hat{\phi}_F^-(t')\right]$,

$$\begin{aligned} \left[\hat{\phi}_F^+(t), \hat{\phi}_F^-(t')\right] &= \int \mathrm{d}^3\boldsymbol{k} \int \mathrm{d}^3\boldsymbol{k}' \frac{\widetilde{F}(\boldsymbol{k})^* \widetilde{F}(\boldsymbol{k}')}{2(2\pi)^3\sqrt{\omega_{\boldsymbol{k}}\omega_{\boldsymbol{k}'}}} e^{\mathrm{i}\omega_{\boldsymbol{k}}(t-t')} \left[\hat{a}_{\boldsymbol{k}}, \hat{a}_{\boldsymbol{k}'}^\dagger\right] \\ &= \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3\omega_{\boldsymbol{k}}} |\widetilde{F}(\boldsymbol{k})|^2 e^{\mathrm{i}\omega_{\boldsymbol{k}}(t-t')} \mathbb{I} . \end{aligned} \tag{B.8}$$

Two terms will vanish, $\left[\hat{\phi}_F^+(t), \hat{\phi}_F^+(t')\right] = \left[\hat{\phi}_F^-(t), \hat{\phi}_F^-(t')\right] = 0$, and the fourth is the conjugate of this one. Both terms are proportional to the identity, therefore its sum $\left[\hat{\phi}_F(t), \hat{\phi}_F(t')\right]$ too. Also, substituting,

$$\theta = \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3\omega_{\boldsymbol{k}}} |\widetilde{F}(\boldsymbol{k})|^2 \int \mathrm{d}t \int^t \mathrm{d}t' \chi(t)\chi(t') \operatorname{Im}\left\{e^{\mathrm{i}\omega_{\boldsymbol{k}}(t-t')}\right\} . \tag{B.9}$$

which is means θ is a real phase. This completes the proof of the two intended results and consequently of Eq. (B.5).

B.1 Characteristic function of work

Here we calculate the work characteristic function for KMS states, which contains all the statistics. The expression for the characteristic function is (4.1). First we particularize it to our family of processes, using the closed-form expression in (B.5).

$$\widetilde{P}(\mu) = \left\langle e^{\mathrm{i}\lambda\hat{\phi}_{\chi F}} e^{\mathrm{i}\mu\hat{H}_0} e^{-\mathrm{i}\lambda\hat{\phi}_{\chi F}} e^{-\mathrm{i}\mu\hat{H}_0} \right\rangle_\beta . \tag{B.10}$$

We want to use Wick's theorem to evaluate the expectation. We first have to convert the content of the expectation to an exponential of a sum of integrated field operators. The first step in this direction is:

$$\begin{aligned} e^{\mathrm{i}\mu\hat{H}_0} e^{-\mathrm{i}\lambda\hat{\phi}_{\chi F}} e^{-\mathrm{i}\mu\hat{H}_0} &= \exp\left\{-\mathrm{i}\lambda \int \mathrm{d}t \chi(t) e^{\mathrm{i}\mu\hat{H}_0} \hat{\phi}_F(t) e^{-\mathrm{i}\mu\hat{H}_0}\right\} \\ &= \exp\left\{-\mathrm{i}\lambda \int \mathrm{d}t \chi(t) \hat{\phi}_F(t+\mu)\right\} \\ &= e^{-\mathrm{i}\lambda\hat{\phi}_{\gamma F}} , \end{aligned} \tag{B.11}$$

with $\gamma(t) = \chi(t-\mu)$. We use the BCH formula to get:

$$\left\langle e^{\mathrm{i}\lambda\hat{\phi}_{\chi F}} e^{-\mathrm{i}\lambda\hat{\phi}_{\gamma F}} \right\rangle_\beta = e^{\frac{1}{2}\lambda^2 \left\langle \left[\hat{\phi}_{\chi F}, \hat{\phi}_{\gamma F}\right] \right\rangle} \left\langle e^{\mathrm{i}\lambda(\hat{\phi}_{\chi F} - \hat{\phi}_{\gamma F})} \right\rangle_\beta , \tag{B.12}$$

where again the higher order commutators vanished thanks to $\left[\hat{\phi}_F(t), \hat{\phi}_F(t')\right] \propto \mathbb{I}$. Now we can apply Wick's theorem to evaluate what is left,

$$\left\langle e^{\mathrm{i}\lambda(\hat{\phi}_{\chi F} - \hat{\phi}_{\gamma F})} \right\rangle_\beta = e^{-\frac{1}{2}\lambda^2 \left\langle \left(\hat{\phi}_{\chi F} - \hat{\phi}_{\gamma F}\right)^2 \right\rangle_\beta} , \tag{B.13}$$

We will get the characteristic function in terms of integrated Wightman functions, as in the former calculation for the energy difference. $\left\langle (\hat{\phi}_{\chi F})^2 \right\rangle_\beta$ and $\left\langle (\hat{\phi}_{\gamma F})^2 \right\rangle_\beta$ have the same value, because the Wightman is stationary and γ is a time-shifted version of χ. Joining everything together the characteristic function is

$$\left\langle e^{\mathrm{i}\lambda\hat{\phi}_{\chi F}} e^{-\mathrm{i}\lambda\hat{\phi}_{\gamma F}} \right\rangle_\beta = e^{\lambda^2 \left(\left\langle \hat{\phi}_{\chi F} \hat{\phi}_{\gamma F} \right\rangle_\beta - \left\langle (\hat{\phi}_{\chi F})^2 \right\rangle_\beta \right)} , \tag{B.14}$$

where in terms of Wightman functions

$$\left\langle \hat{\phi}_{\chi F}\hat{\phi}_{\gamma F}\right\rangle_\beta - \left\langle (\hat{\phi}_{\chi F})^2\right\rangle_\beta = \int \mathrm{d}t\chi(t)\int \mathrm{d}^3\boldsymbol{x}F(\boldsymbol{x})\int \mathrm{d}t'\chi(t')\int \mathrm{d}^3\boldsymbol{x}'F(\boldsymbol{x}')(\mathcal{W}_\beta(t,x,t'+\mu,\boldsymbol{x}')-\mathcal{W}_\beta(t,x,t',\boldsymbol{x} \tag{B.15}$$

The exact expression for the characteristic function of work for thermal states arises after substituting the value of the Wightman functions (B.24),

$$\widetilde{P}(\mu) = \exp\left\{\lambda^2\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3\omega_{\boldsymbol{k}}}|\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2|\widetilde{F}(\boldsymbol{k})|^2\left(\mathrm{i}\sin\omega_{\boldsymbol{k}}\mu + \frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}(\cos\omega_{\boldsymbol{k}}\mu - 1)\right)\right\} \tag{B.16}$$

Which matches with the perturbative expression found in [8], by expanding on lambda. However, this analytic expression provides all the higher orders, while the perturbative expression was truncated at order λ^2.

B.2 Internal energy difference distribution and operator

Here we calculate the characteristic function of energy difference for initial KMS states, which will give us access to all the moments of the energy difference. Its expression is [4]

$$\widetilde{P}_{\Delta\hat{U}}(\mu) = \left\langle e^{\mathrm{i}\mu\Delta\hat{U}}\right\rangle_\beta . \tag{B.17}$$

Where β indicates the inverse temperature of the KMS state. First, we compute a general non-perturbative expression for the energy difference $\Delta\hat{U} = \hat{U}^\dagger\hat{H}_0\hat{U} - \hat{H}_0$ and then we will substitute it into the characteristic function formula.

The evolution unitary acts as a displacement $\hat{D}_\alpha$ with $\alpha(\boldsymbol{k}) = -\mathrm{i}\lambda\frac{\widetilde{\chi}(\omega_{\boldsymbol{k}})\widetilde{F}(\boldsymbol{k})^*}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}}$, because of Eq. (B.5). The free Hamiltonian is a combination of annihilation and creation operators, $\int \mathrm{d}^3\boldsymbol{k}\omega_{\boldsymbol{k}}\hat{a}^\dagger_{\boldsymbol{k}}\hat{a}_{\boldsymbol{k}}$, and it is known how displacement operators act over ladder operators [40],

$$\hat{D}^\dagger_\alpha\hat{a}_{\boldsymbol{k}}\hat{D}_\alpha = \hat{a}_{\boldsymbol{k}} + \alpha(\boldsymbol{k})\mathbb{I}\,, \tag{B.18}$$

$$\hat{U}^\dagger \hat{H}_0 \hat{U} = \int \mathrm{d}^3\boldsymbol{k}\omega_{\boldsymbol{k}}\left(\hat{a}^\dagger_{\boldsymbol{k}}\hat{a}_{\boldsymbol{k}} + \alpha(\boldsymbol{k})\hat{a}^\dagger_{\boldsymbol{k}} + \alpha(\boldsymbol{k})^*\hat{a}_{\boldsymbol{k}} + |\alpha(\boldsymbol{k})|^2\mathbb{I}\right). \tag{B.19}$$

We identify that $\int \mathrm{d}^3\boldsymbol{k}\omega_{\boldsymbol{k}}(\alpha(\boldsymbol{k})\hat{a}^\dagger_{\boldsymbol{k}} + \alpha(\boldsymbol{k})^*\hat{a}_{\boldsymbol{k}})$ is proportional to $\dot{\hat{\phi}}_{\chi F}$, the integrated time derivative of the field operator,

$$\dot{\hat{\phi}}_{\chi F} = \int \frac{\mathrm{d}^3\boldsymbol{k}\sqrt{\omega_{\boldsymbol{k}}}}{\sqrt{2(2\pi)^3}}\left(\mathrm{i}\widetilde{\chi}(\omega_{\boldsymbol{k}})\widetilde{F}(\boldsymbol{k})^*\hat{a}^\dagger_{\boldsymbol{k}} - \mathrm{i}\widetilde{\chi}(\omega_{\boldsymbol{k}})^*\widetilde{F}(\boldsymbol{k})\hat{a}_{\boldsymbol{k}}\right). \tag{B.20}$$

Gathering everything the operator of work can be written as

$$\Delta\hat{U} = \hat{U}^\dagger \hat{H}_0 \hat{U} - \hat{H}_0 = -\lambda\dot{\hat{\phi}}_{\chi F} + \lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}|\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2\left|\widetilde{F}(\boldsymbol{k})\right|^2\mathbb{I}. \tag{B.21}$$

Now we come back to computing the characteristic function. The term of $\Delta\hat{U}$ proportional to the identity will give an expectation independent of the state. We are left to evaluate $\left\langle e^{-i\mu\lambda\dot{\hat{\phi}}_{\chi F}}\right\rangle_\beta$, Wick's theorem gives us the answer [?]:

$$\left\langle e^{-i\mu\lambda\dot{\hat{\phi}}_{\chi F}}\right\rangle_\beta = e^{-\frac{1}{2}\mu^2\lambda^2\left\langle\left(\dot{\hat{\phi}}_{\chi F}\right)^2\right\rangle_\beta} \tag{B.22}$$

The expectation $\left\langle\left(\dot{\hat{\phi}}_{\chi F}\right)^2\right\rangle_\beta$ is related to the KMS state Wightman function $\mathcal{W}_\beta(t,x,t',\boldsymbol{x}') = \left\langle\hat{\phi}(t,\boldsymbol{x})\hat{\phi}(t',\boldsymbol{x}')\right\rangle_\beta$. Precisely, we commute the time derivatives and the expectation to get

$$\left\langle\left(\dot{\hat{\phi}}_{\chi F}\right)^2\right\rangle_\beta = \int \mathrm{d}t\chi(t)\int \mathrm{d}^3\boldsymbol{x}F(\boldsymbol{x})\int \mathrm{d}t'\chi(t')\int \mathrm{d}^3\boldsymbol{x}'F(\boldsymbol{x}')\partial_t\partial_{t'}\mathcal{W}_\beta(t,x,t',\boldsymbol{x}') \tag{B.23}$$

And using the expression of the Wightman function for a thermal state [40],

$$\mathcal{W}_\beta(t,x,t',\boldsymbol{x}') = \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3\omega_{\boldsymbol{k}}(e^{\beta\omega_{\boldsymbol{k}}}-1)}\left(e^{\beta\omega_{\boldsymbol{k}}}e^{\mathsf{ik}\cdot(\mathsf{x}-\mathsf{x}')} + e^{-\mathsf{ik}\cdot(\mathsf{x}-\mathsf{x}')}\right). \tag{B.24}$$

The exact expression of the characteristic function of energy difference results from assembling the calculations,

$$\left\langle e^{\mathrm{i}\mu\Delta\hat{U}}\right\rangle_\beta = \exp\left\{\lambda^2\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}|\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2\left|\widetilde{F}(\boldsymbol{k})\right|^2\left(\mathrm{i}\mu - \frac{1}{2}\mu^2\omega_{\boldsymbol{k}}\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\right)\right\}. \tag{B.25}$$

B.3 Table of work and internal energy difference moments

Moment	Energy difference	Work (Ramsey scheme)
Mean	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2$	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2$
Second	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}} +\lambda^4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^2$	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}} +\lambda^4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^2$
Third	$3\lambda^4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)\times\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right) +\lambda^6\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^3$	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\omega_{\boldsymbol{k}}^2 +3\lambda^4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)\times\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right) +\lambda^6\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^3$
Fourth	$3\lambda^4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)^2 +6\lambda^6\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)\times\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^2 +\lambda^8\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^4$	$\lambda^2 \int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}^3 +\lambda^4\left[4\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\omega_{\boldsymbol{k}}^2\right)\times\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right) +3\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)^2\right] +6\lambda^6\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\frac{e^{\beta\omega_{\boldsymbol{k}}}+1}{e^{\beta\omega_{\boldsymbol{k}}}-1}\omega_{\boldsymbol{k}}\right)\times\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^2 +\lambda^8\left(\int \frac{\mathrm{d}^3\boldsymbol{k}}{2(2\pi)^3}\lvert\widetilde{\chi}(\omega_{\boldsymbol{k}})\rvert^2\lvert\widetilde{F}(\boldsymbol{k})\rvert^2\right)^4$

B.4 Perturbative calculation of energy difference expectation in vacuum state

In this appendices we present two ways to compute the statistics of energy difference for quantum fields and the family of unitaries of Eq. (4.16). Here we do it perturbatively, as in [8]. For the calculation to remain manageable, we restrict ourselves to the expectation on the vacuum state $|\Omega\rangle$ of the quantum field.

The starting point is to get rid of the time ordering operator in the unitaries. We perform a Dyson expansion of $\hat{U}$ on λ to remove it. Then we keep track of up to fourth degree in λ,

$$\hat{U} = \mathbb{I} + \hat{U}^{(1)} + \hat{U}^{(2)} + \hat{U}^{(3)} + \hat{U}^{(4)} + \mathcal{O}\big(\lambda^5\big) \tag{B.26}$$

$$\hat{U}^{(1)} = -\mathrm{i}\int \mathrm{d}t H_I(t) \qquad \hat{U}^{(2)} = -\int \mathrm{d}t \int^t \mathrm{d}t' H_I(t)H_I(t') \qquad \hat{U}^{(3)} = \mathrm{i}\int \mathrm{d}t \int^t \mathrm{d}t' \int^{t'} \mathrm{d}t'' H_I(t)H_I(t')H_I \tag{B.27}$$

Where we defined $\hat{H}_I = \hat{H} - \hat{H}_{free}$ with $\hat{H}$ the system Hamiltonian, shown in (3.1). The superindex indicates the degree in λ because $H_I \propto \lambda$. We did not gave the expression for $\hat{U}^{(4)}$ because we will not use it. Obtain an approximate energy difference operator by expanding

$$\Delta\hat{U} = \Big(\mathbb{I} + \hat{U}^{(1)} + \hat{U}^{(2)} + \hat{U}^{(3)} + \hat{U}^{(4)}\Big)^\dagger \hat{H}_0\Big(\mathbb{I} + \hat{U}^{(1)} + \hat{U}^{(2)} + \hat{U}^{(3)} + \hat{U}^{(4)}\Big) - \hat{H}_0 + \mathcal{O}\big(\lambda^5\big)\,. \tag{B.28}$$

The vacuum state expectation of most terms is zero, because $\hat{H}_0\,|\Omega\rangle = 0$, leaving

$$\begin{aligned}\Big\langle \Delta\hat{U}\Big\rangle_\Omega = {} & \Big\langle \hat{U}^\dagger Order1 \hat{H}_0 \hat{U}^{(1)}\Big\rangle_\Omega \\ & + \Big\langle \hat{U}^\dagger Order2 \hat{H}_0 \hat{U}^{(2)}\Big\rangle_\Omega + 2\,\mathrm{Re}\Big\{\Big\langle \hat{U}^\dagger Order1 \hat{H}_0 \hat{U}^{(3)}\Big\rangle_\Omega\Big\} \\ & + \mathcal{O}\big(\lambda^5\big)\,.\end{aligned} \tag{B.29}$$

We now show the calculation of one expectation, the rest can be performed in a similar way.

$$\Big\langle \hat{U}^\dagger Order2 \hat{H}_0 \hat{U}^{(2)}\Big\rangle_\Omega = \lambda^4 \int \mathrm{d}t_1 \chi(t_1) \int^{t_1} \mathrm{d}t_2 \chi(t_2) \int \mathrm{d}t_3 \chi(t_3) \int^{t_3} \mathrm{d}t_4 \chi(t_4) \Big\langle \hat{\phi}_F(t_1)\hat{\phi}_F(t_2)\hat{H}_0\hat{\phi}_F(t_3)\hat{\phi}_F(t_4 \tag{B.30}$$

Split the field operators

$$\hat{\phi}_F(t) = \hat{\phi}_F^+(t) + \hat{\phi}_F^-(t) \qquad \hat{\phi}_F^+(t) = \int \frac{\mathrm{d}^3\boldsymbol{k}}{\sqrt{2(2\pi)^3\omega_{\boldsymbol{k}}}} \widetilde{F}(\boldsymbol{k})^* e^{\mathrm{i}\omega_{\boldsymbol{k}} t}\hat{a}_{\boldsymbol{k}}^\dagger \qquad \hat{\phi}_F^- = \hat{\phi}_F^{+\dagger}\,. \tag{B.31}$$

Then it turns out that

$$\left\langle \hat{\phi}_F(t_1)\hat{\phi}_F(t_2)\hat{H}_0\hat{\phi}_F(t_3)\hat{\phi}_F(t_4)\right\rangle_\Omega = \left\langle \hat{\phi}_F^-(t_1)\hat{\phi}_F^-(t_2)\hat{H}_0\hat{\phi}_F^+(t_3)\hat{\phi}_F^+(t_4)\right\rangle_\Omega , \tag{B.32}$$

which can be evaluated using

$$\left\langle \hat{a}_{\boldsymbol{k}}\hat{a}_{\boldsymbol{k}'}\hat{H}_0\hat{a}^\dagger_{\boldsymbol{k}''}\hat{a}^\dagger_{\boldsymbol{k}'''}\right\rangle_\Omega = (\omega_{\boldsymbol{k}}+\omega_{\boldsymbol{k}'})\left\langle \hat{a}_{\boldsymbol{k}}\hat{a}_{\boldsymbol{k}'}\hat{a}^\dagger_{\boldsymbol{k}''}\hat{a}^\dagger_{\boldsymbol{k}'''}\right\rangle_\Omega = (\omega_{\boldsymbol{k}}+\omega_{\boldsymbol{k}'})[\delta(\boldsymbol{k}-\boldsymbol{k}'')\delta(\boldsymbol{k}'-\boldsymbol{k}''')+\delta(\boldsymbol{k}-\boldsymbol{k}''')\delta(\boldsymbol{k}'- \tag{B.33}$$

The evaluation gives that $\left\langle \hat{\phi}_F(t_1)\hat{\phi}_F(t_2)\hat{H}_0\hat{\phi}_F(t_3)\hat{\phi}_F(t_4)\right\rangle_\Omega$ is equal to

$$\int \frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k}'}{(2\pi)^6 2^2}\left|\widetilde{F}(\boldsymbol{k})\right|^2\left|\widetilde{F}(\boldsymbol{k}')\right|^2\frac{\omega_{\boldsymbol{k}}+\omega_{\boldsymbol{k}'}}{\omega_{\boldsymbol{k}}\omega_{\boldsymbol{k}'}}\left(e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_3)+\omega_{\boldsymbol{k}'}(t_2-t_4)]}+e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_4)+\omega_{\boldsymbol{k}'}(t_2-t_3)]}\right) , \tag{B.34}$$

which can be substituted back to Eq. (B.30) to get $\left\langle \hat{U}^\dagger Order2\hat{H}_0\hat{U}^{(2)}\right\rangle_\Omega$. Calculating the two remaining expectations provides

$$\begin{aligned}
&\left\langle \Delta\hat{U}\right\rangle_\Omega = \\
&\quad\lambda^2\int\frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3 2}|\widetilde{\chi}(\omega_{\boldsymbol{k}})|^2\left|\widetilde{F}(\boldsymbol{k})\right|^2 \\
&+\lambda^4\int\int\frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k}'}{(2\pi)^6 2^2}\left|\widetilde{F}(\boldsymbol{k})\right|^2\left|\widetilde{F}(\boldsymbol{k}')\right|^2\frac{\omega_{\boldsymbol{k}}+\omega_{\boldsymbol{k}'}}{\omega_{\boldsymbol{k}}\omega_{\boldsymbol{k}'}}\int\mathrm{d}t_1\chi(t_1)\int^{t_1}\mathrm{d}t_2\chi(t_2)\int\mathrm{d}t_3\chi(t_3) \\
&\quad\times\int^{t_3}\mathrm{d}t_4\chi(t_4)\left(e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_3)+\omega_{\boldsymbol{k}'}(t_2-t_4)]}+e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_4)+\omega_{\boldsymbol{k}'}(t_2-t_3)]}\right) \\
&-\lambda^4\int\int\frac{\mathrm{d}^3\boldsymbol{k}\mathrm{d}^3\boldsymbol{k}'}{(2\pi)^6 2^2}\left|\widetilde{F}(\boldsymbol{k})\right|^2\left|\widetilde{F}(\boldsymbol{k}')\right|^2\frac{1}{\omega_{\boldsymbol{k}}}\int\mathrm{d}t_1\chi(t_1)\int^{t_1}\mathrm{d}t_2\chi(t_2)\int^{t_2}\mathrm{d}t_3\chi(t_3)\int\mathrm{d}t_4\chi(t_4) \\
&\quad\times 2\,\mathrm{Re}\left\{e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_3)+\omega_{\boldsymbol{k}'}(t_2-t_4)]}+e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_2-t_3)+\omega_{\boldsymbol{k}'}(t_1-t_4)]}+e^{-\mathrm{i}[\omega_{\boldsymbol{k}}(t_1-t_2)+\omega_{\boldsymbol{k}'}(t_3-t_4)]}\right\} \\
&+\mathcal{O}\left(\lambda^6\right)
\end{aligned} \tag{B.35}$$

which contradicts the non-perturbative calculation in Appendix B.2. The exact expectation value only has degree two on λ, there must not be any fourth degree term neither higher in λ. Consistency remains because the fourth degree terms do cancel out in the way presented in the main text's section 4.2.3.